

Structural and biological control of the Cenozoic epithermal uranium concentrations from the Sierra Peña Blanca, Mexico

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Received: 5 February 2011 / Accepted: 6 February 2012 / Published online: 23 February 2012
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Abstract Epithermal uranium deposits of the Sierra Peña Blanca are classic examples of volcanic-hosted deposits and have been used as natural analogs for radionuclide migration in volcanic settings. We present a new genetic model that incorporates both geochemical and tectonic features of these deposits, including one of the few documented cases of a geochemical signature of biogenic reducing conditions favoring uranium mineralization in an epithermal deposit. Four tectono-magmatic faulting events affected the volcanic pile. Uranium occurrences are associated with breccia zones at the intersection of fault systems. Periodic reactivation of these structures associated with Basin and Range and Rio Grande tectonic events resulted in the mobilization of U and

other elements by meteoric fluids heated by geothermal activity. Focused along breccia zones, these fluids precipitated under reducing conditions several generations of pyrite and uraninite together with kaolinite. Oxygen isotopic data indicate a low formation temperature of uraninite, 45–55°C for the uraninite from the ore body and ~20°C for late uraninite hosted by the underlying conglomerate. There is geochemical evidence for biological activity being at the origin of these reducing conditions, as shown by low $\delta^{34}\text{S}$ values (~–24.5‰) in pyrites and the presence of low $\delta^{13}\text{C}$ (~–24‰) values in microbial patches intimately associated with uraninite. These data show that tectonic activity coupled with microbial activity can play a major role in the formation of epithermal uranium deposits in unusual near-surface environments.

Editorial handling: M. Cuney

Electronic supplementary material The online version of this article (doi:10.1007/s00126-012-0408-5) contains supplementary material, which is available to authorized users.

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Keywords Uranium deposits · Epithermal deposits · Silicic volcanics · Biogenic activity · Stable isotope geochemistry · Geothermal systems · Cenozoic tectonics · Breccias

Introduction

Volcanic-type deposits are an important geological target for uranium exploration (e.g., Streltsova caldera; Chabiron et al. 2003). These deposits can be structurally controlled and/or stratabound within volcanic host rocks of high silica to intermediate composition. In epithermal deposits, uranium is accompanied by Mo and minor Cu, Se, and F. Among these uranium volcanic-hosted deposits, the Peña Blanca Mo–U field with over 100 airborne anomalies is an important uranium province in northern Mexico, about 50 km north of Chihuahua City. This district is reported as hosting 13,000 t Mo reserves (Goodell et al. 1979) and 1,000–2,500 t U (I.A.E.A. 2009). Several deposits, located at the

volcanic limestone contact, have been recognized by extensive drilling programs. For example, the Nopal I and Las Margaritas mines have been mined by underground or open-pit mining, during the 1970s and 1980s (Goodell 1981). In addition, similarities in geologic and climatic conditions between the Nopal I uranium deposit and the Yucca Mountain site, once proposed for geologic disposal of high-level nuclear waste, have provided ways of testing long-term total system performance assessment models (e.g., Ildefonse et al. 1990; Janeczek et al. 1996; Ewing 1999; Murphy 2000), such as the alteration conditions and radionuclide transport in the unsaturated zone (Percy et al. 1994; Reyes-Cortés 1997; Calas et al. 2008).

The genesis of the Peña Blanca uranium deposits, including the origin of the ore-forming fluids (Aniel-George et al. 1991; Percy et al. 1994; Pickett and Murphy 1997; Prikryl et al. 1997; Calas et al. 2008), and its association with the regional geologic history remain poorly constrained and controversial. Several models have been proposed (e.g., Calas 1977; Aniel and Leroy 1985; Ildefonse et al. 1990). In particular, it has been difficult to constrain the age of primary mineralization, which consists of fine-grained uraninite (~1–100 μm) (Percy et al. 1994; Fayek et al. 2006). These problems are further magnified by the susceptibility of uraninite to alteration and radiation damage (Finch and Ewing 1992; Janeczek and Ewing 1995).

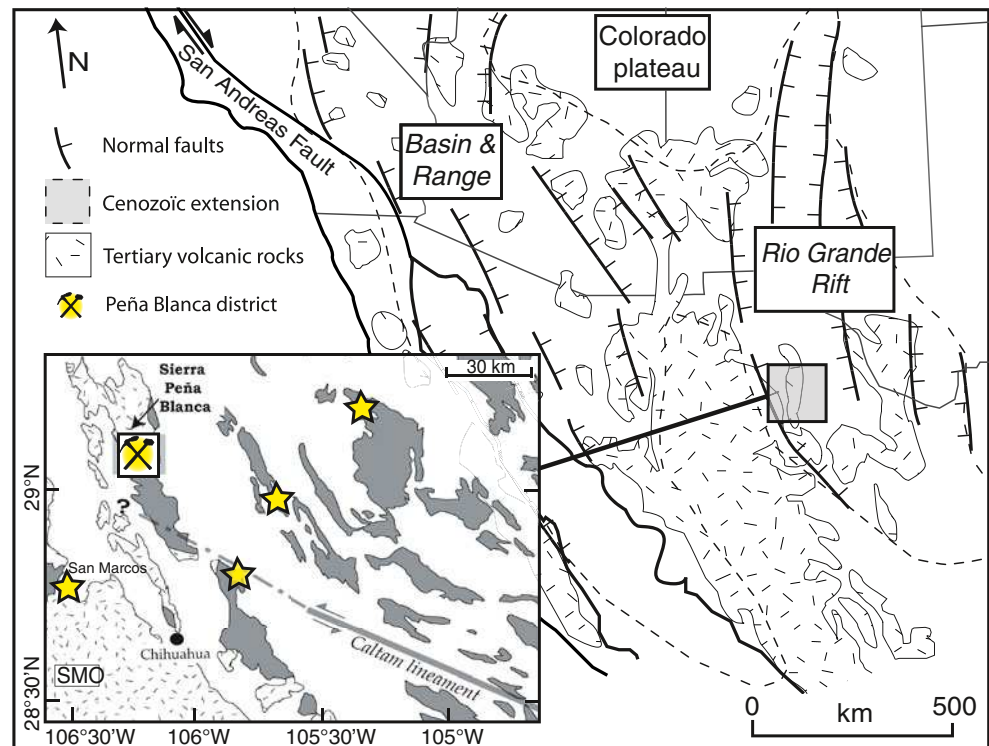
By refining the tectonic history of the Peña Blanca uranium district and on the basis of a set of drill core and outcrop sampling, we propose a 3D description of deposit

formation. We develop a tectonic model that rationalizes the formation and post-depositional modification of the epithermal deposits of the Peña Blanca uranium district. There is isotopic evidence that deposit formation has been assisted by a biological mediation, favoring local reducing conditions at the origin of the precipitation of the primary U mineralization and the accompanying sulfides. These original conditions shed light on the formation processes of epithermal deposits resulting from the circulation of meteoric waters.

Geological setting

The Sierra Peña Blanca is an 80-km-long NNW striking block on the eastern edge of the Sierra Madre Occidental plateau (SMO), the largest Cenozoic silicic igneous province in the world (Ferrari et al. 2007) (Fig. 1). The volcanic emissions in the SMO occurred at the transition between a compressional regime (associated with the subduction of the Farallon plate beneath North America to the West) and an extensional regime (leading to the opening of the Gulf of California with emission of peralkaline lavas; McDowell and Clabaugh 1979; Ferrari et al. 2007). Lateral stratigraphic variability results in discrepancies in the stratigraphy of the Sierra Peña Blanca (e.g., Chavez and Iza 1975; Goodell 1981; Magonthier 1987). The volcanic units (from Nopal Formation to Mesa Formation) consist of more than 400 m of welded and devitrified ash-fall and ash-flow tuffs with

Fig. 1 A map showing middle to late Cenozoic lithospheric extension and the location of the Peña Blanca district (modified from Eaton 1982). The stars (see inset) indicate other uranium concentrations in the vicinity of the Peña Blanca district. Gray shaded outcrops are Cretaceous sedimentary rocks (inset)



intercalated thin vitrophyric layers. Ash-flow deposits are mixed with conglomerates, mostly made of remobilized fresh volcanic material, which have been deposited in paleovalleys during lulls in volcanic activity. The volcanic pile is composed of three units where K–Ar dating of feldspars (Alba and Chavez 1974) gave ages of 44.0 ± 0.9 Ma (recalculated age) for the Nopal Formation, 38.3 ± 0.8 Ma for the Escuadra Formation, and 37.3 ± 0.7 Ma for the Mesa Formation. Conglomerates of the Pozos Formation, composed of calcareous and volcanic blocks, lie unconformably between the gently folded Cretaceous limestone rocks of the Edwards Formation and the overlying volcanic sequence.

The Basin and Range extensional event (Eaton 1982; Henry and Aranda-Gomez 1992; Nieto-Samaniego et al. 1999) affected the entire volcanic sequence at Peña Blanca. It is characterized by NW–NNW striking tectonic blocks (Henry and Price 1986; Fig. 1), which created NNW striking wide basins, separated by narrow, isolated ranges. These ranges, which are the northern extension of the Laramidian fold-and-thrust belt folds of the Sierra Madre Oriental (Tardy et al. 1989), exhibit folded sedimentary rocks, mostly Cretaceous limestone rocks (Stegge 1979).

The Peña Blanca area is situated at the junction between the Basin and Range and the Rio Grande Rift provinces

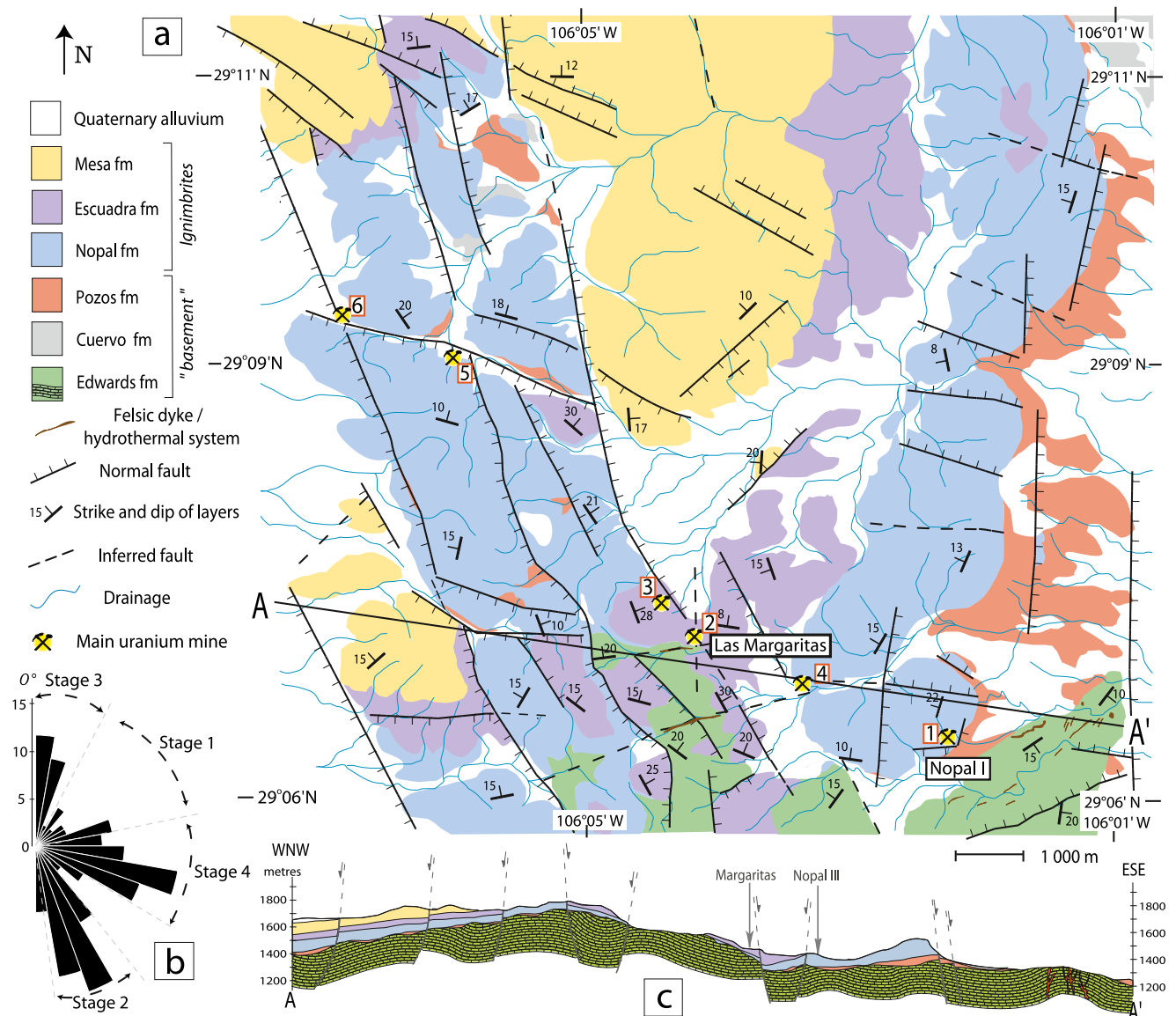


Fig. 2 **a** A detailed structural and geological map of the Peña Blanca uranium district showing the location of the major faults and fracture systems and lithological units and of the uranium mines and occurrences; Nopal I (1), Las Margaritas (2), Puerto III (3), Nopal III (4), Puerto II (5), and Puerto 0 (6). **b** Rose diagram compilation of field

measurement strikes of all the faults and fractures measured from the Peña Blanca uranium district ($n=124$). **c** Cross section through the Peña Blanca uranium district showing the major faults that affect the region. Nopal III and Las Margaritas deposits are shown for reference

(RGR; Fig. 1). The RGR consists of a series of deep en echelon N–S grabens extending over 1,000 km from central Colorado to west Texas and northern Chihuahua State, Mexico (Chapin 1979; Keller and Cather 1994). In the southern part of the RGR, Seager et al. (1984) reported two episodes of rifting: an early rifting stage at ~20 Ma producing broad basins and a late, more intense episode of rifting at 10–3 Ma, which increased the overall extension and modified the topography. Tardy et al. (1989) described a N120 strike-slip crustal-scale tectonic feature in the region called the “Caltam lineament.” A kinematic interpretation is suggested by a sinistral shift and apparent rotation of Larmanian folds along eastern Chihuahua (Fig. 1, inset). This lineament disappears westwards where it is covered by the thick SMO volcanic sequence, suggesting a decrease in activity during Cenozoic times.

Structure and tectonics

Field mapping, combined with a *Digital Elevation Model* analysis based on the data of the Shuttle Radar Topography Mission (USGS 2004), resulted in a detailed integrated regional structural analysis of the area that incorporates the distribution of uranium occurrences (Fig. 2a). Four generations of fault networks (Fig. 2b) affected all Peña Blanca units in this area (from Edwards Formation to Mesa Formation) and created tilted blocks with various orientations (Fig. 2c). A subvertical set of fractures and faults in Cretaceous rocks with a strike of N40 to N70 is poorly developed in the overlying units, and are therefore referred to as stage 1 faults. In the southeast part of the study area (Fig. 2a), a series of NE to ENE striking andesitic dyke swarms intrudes the Cretaceous limestone. Dykes, 0.1 to 10 m wide, occur discontinuously in fractures that are parallel to stage 1 faults. Extensive calcite crystallization and skarn formation are associated with these dykes, which are the first evidence of intrusive rocks in the Peña Blanca district. Although these dykes crosscut the limestone, it is unclear whether they crosscut the volcanic rocks. Locally, normal-movement slickenlines associated with these dykes suggest reactivation during later extensive Cenozoic events.

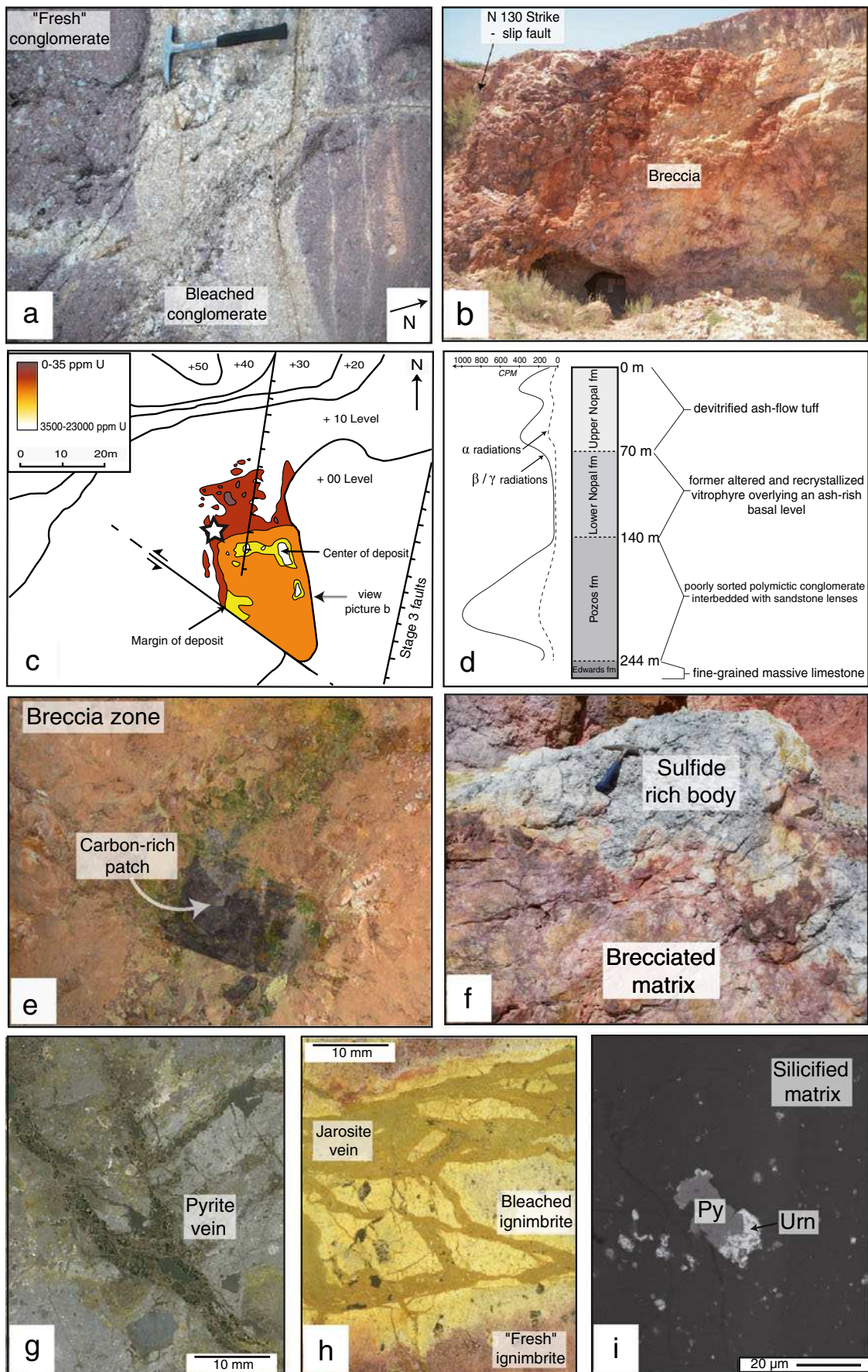
Subparallel faults trending N150 to N175 (dip ranging from 60° to 90°; stage 2) are dominant in the western margin of the Sierra Peña Blanca. They create an asymmetric horst (Fig. 2a) coincident with the NNW–SSE regional orientation associated with Basin and Range tectonics, which started as early as 30 Ma and lasted until 10 Ma (Eaton 1982). N to NNE subvertical stage 3 faults form echelon sets of fault blocks along the eastern margin of the Sierra Peña Blanca with only a minimal displacement (Fig. 2a). These faults are related to the development of the southern extension of Rio Grande Rift after 30 Ma (e.g., Chapin 1979).

N95 to N130 stage 4 vertical faults cut across the entire stratigraphic column and offset both stage 2 and stage 3 fault systems (Fig. 2b). Locally, a late sinistral strike-slip movement accompanies the widespread normal movement of these faults. This fault system is accompanied by rock bleaching and calcite crystallization indicating fluid circulation in fractures (Fig. 3a). The preexisting “Caltam lineament” (Fig. 1, inset) may have acted as a weak lithospheric zone, accommodating late Cenozoic extension and providing a conduit for later magmatism and emplacement of underlying intrusive complexes (Chaulot-Talmon 1984). Some similarities may be found with the San Marcos uranium deposit (Reyes-Cortés 1997), which is linked with a caldera developed in an alkaline complex, located 50 km west of the Sierra de Peña Blanca and dated at 45–46 Ma.

Mineralized outcrops

Hand samples were collected from both mineralized and unmineralized outcrops as well as a drill core from the Nopal I uranium deposit to compare unaltered rocks and rocks associated with uranium mineralization in three dimensions. Twenty-two samples were collected from 250 m of drill core recovered from a diamond drill hole (DDH-PB1) drilled through the Nopal I deposit. Based on petrographic observations, the drill core can be divided into four main units: (1) Upper Nopal fm (0–70 m), (2) Lower Nopal fm (70–140 m), (3) Pozos fm conglomerates (140–244 m), and (4) the Cretaceous limestones from the Edwards fm (244–250 m; Fig. 3d). The entire core is highly brecciated, bleached, and recrystallized. In zones of intense brecciation, feldspars are altered to clay minerals and the matrix is highly silicified. Void spaces and fractures, subparallel to the drill core axis, occur along the entire length of the core.

Fig. 3 **a** Bleached N095 sinistral fault (stage 4) offsetting N000 bleached fracture (stage 3), in the Pozos Formation; **b** Breccia zones and adit entrance at the Nopal I deposit showing increased alteration towards the N130 fault; **c** Plan view of the Nopal I deposit showing the uranium-rich zones, the location of the drill core characterized in this study (*star*), and the major fault systems; **d** A schematic cross section of the PB-1 drill core from the Nopal I deposit, correlated with a radiation log of the core, where the α counts are largely produced by ^{235}U , and β/γ counts are produced by ^{238}U ; **e** Carbon-rich patch (15 cm high) within the high-grade breccia zone from Nopal I mine; **f** Brecciated matrix and sulfide-rich body exposed in the Las Margaritas open pit; **g** Polished thin section of a highly silicified and pyrite-rich matrix from the Pozos Formation sample in Nopal I drill core; **h** Polished thin section of a highly brecciated rock sampled away of the mines area within the upper Nopal Formation, 500 m east of location 5 (Fig. 2a). Ignimbrite matrix is bleached and brecciated by yellow fine-grained jarosite vein; **i** Backscattered electron scanning electron microscopy (SEM) image of a stage B pyrite (Py)-uraninite (Urn) association within silicified ignimbrite matrix from the drill core of the Nopal I deposit



Calcite veinlets (1 to 4 cm wide) occur in the Pozos Formation and close to the Edwards fm, and less commonly in the Nopal Formation.

The stratigraphic control of the mineralization is illustrated by 85% of uranium occurrences being located within the lower part of the volcanic pile (70% in Nopal Formation and 15% in Escuadra Formation). Uranium mineralization is associated with tectonic breccias, although locally hydraulic brecciation may have been present. These brecciated zones are widespread throughout the mining district, at the intersection of at least two of the major fault systems described above. Three occurrences are noticeable: Nopal I, Las Margaritas, and Puerto III (Fig. 2a). Nopal I mineralization (Calas 1977; Goodell 1981; Aniel and Leroy 1985; Reyes-Cortés 1997; Dobson et al. 2008), mined during the early 1980s, comprises two exposed levels which provide a three-dimensional view of the structure hosting the uranium mineralization (Fig. 3b). The main ore body consists of a breccia zone, 50×25 m wide that extends 115 m below the surface within the Nopal and Pozos formations (Fig. 3c, d). The blocks constituting this breccia are bleached, silicified, and hematitized. Several 10 to 20-cm-sized carbon patches have been found within the high-grade ore (Fig. 3e), associated with relictual primary uraninite (UO_2) and pyrite. These primary phases have been altered to hematite, goethite, and late U(VI) phases (mostly uranyl silicates and oxyhydroxides). Uranyl minerals occur in between breccia fragments, while clay minerals have formed both between breccia fragments and in the matrix (e.g., Calas 1977; Reyes-Cortés 1997). Mineralization is restricted to the breccia zone, while alteration extends for a few meters into the welded tuff. The mineralized brecciated zone is bound to the east by a network of stage 3 normal faults and to the south by a vertical N130 striking strike-slip sinistral stage 4 fault (Fig. 3c). The youngest fractures cutting the main ore body are lined with secondary U(VI) minerals.

The Las Margaritas deposit is located on the northern margin of a N075 trending stage 1 subvertical fault deep-seated in the Edwards formation. The fault exposes recrystallized and brecciated limestone. The mineralized zone extends discontinuously for a distance of over 2 km along the main N150 striking stage 2 Basin and Range fault network (e.g., Puerto III mine, Fig. 2a). Stage 2 faults have been offset by late stage 3 and stage 4 faults. Consequently, ignimbritic rocks in this area are highly fractured, kaolinized, and silicified. Voids and fractures are commonly lined with iron oxides, especially at the vicinity of sulfide-rich silicified bodies (Fig. 3f). Uranium is not only found in brecciated zone but also disseminated in the volcanic groundmass and in fractures within the underlying limestones (Goodell 1981). In the Las Margaritas deposit, where brecciation and late reactivation of fault networks are more intense than in Nopal I, only oxidized uranium

is found, as U(VI) silicates (mainly α -uranophane, $\text{Ca}(\text{UO}_2)_2\text{Si}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$).

Some sulfide-rich samples from various localities across the Peña Blanca district are characterized by pervasive pyrite grains, disseminated in a silicified brecciated groundmass or precipitated along fractures and voids (Fig. 3g). Oxidation of these pyritized bodies produces intense hematitization of the host rock (Fig. 3b, f). Some of these sulfide-rich bodies are spatially associated with uranium occurrences. In some places, alteration leads to yellow sulfate minerals such as jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) and alunite ($\text{KA}_3(\text{SO}_4)_2(\text{OH})_6$) (Fig. 3h), as along the Rio Grande Rift (Lueth et al. 2005). Alunite and jarosite are more abundant at Las Margaritas than at Nopal I. Their formation is accompanied by an intense matrix silicification, reflecting increasing silica solubility at low pH values, as observed during hot spring-driven argillic alteration in caldera fillings, in which silicites and opalites are accompanied by kaolinite, alunite, and pyrite (Lexa et al. 1999). Hematitized and silicified ignimbrite groundmass may be overprinted by jarosite or alunite along breccia zones and fractures, precipitated from sulfate-rich fluids (Fig. 3h).

Analytical methods

Scanning electron microscopy and electron microprobe analysis

A Cambridge Stereoscan 120 scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS) analyzer was used with a 1- μm beam accelerated at 20 keV. Electron Microprobe CAMECA SX100 was operated at 15 keV, with a sample current of 20 nA, a beam diameter of 1 μm , and counting times of 40 s per element.

High-resolution SEM of the organic-rich samples and pyrite was performed at the Nanofabrication Facility at the University of Western Ontario. Samples were polished and cut into thin wafers (~1 mm thick) that were mounted using 12-mm carbon adhesive tabs. To reduce sample charging, a Filgen osmium plasma coater (OPC 80T) was used to apply a thin layer of osmium metal (3 nm). A LEO (Zeiss) 1540 XB field emission scanning electron microscope, equipped with a quadrant backscattered electron detector, was used to provide information about the chemical composition of the samples and produce high-resolution images at an operating voltage of 10 kV. An Oxford Instruments' INCAx-sight EDS, operating at a voltage of 10 kV, was utilized for elemental analysis

Secondary ion mass spectrometry

The analytical protocol for O-isotope measurements in uraninite using a CAMECA ims 7f secondary ion mass

spectrometry (SIMS) was similar to that described by Fayek et al. (2002). Oxygen isotopic composition of standards and uranium minerals was measured with a CAMECA ims 7f SIMS at the University of Manitoba using a Cs^+ primary beam and monitoring O secondary ions with extreme energy filtering of 200 eV (Riciputi et al. 1998). The ~ 2 -nA primary ion beam was focused to a 10×20 - μm spot using a 100- μm aperture in the primary column. A synthetic uraninite crystal ($\text{UO}_{2.1}$) with a $\delta^{18}\text{O}_{\text{V-SMOW}}$ value of $8.1 \pm 0.3\%$ was used to correct for instrumental mass fractionation (IMF). The synthetic uraninite was made by Atomic Energy Canada Ltd. in the late 1940s. The sample is described briefly in (Fayek et al. 2002). The spot-to-spot reproducibility on the UO_2 standard was $\pm 0.5\%$ (1σ). The overall precision and accuracy for each isotope analysis include errors arising from counting statistics of each individual analysis, calibration to a known standard, and uncertainty in deadtime corrections arising from variable count rates. In general, the overall precision was $\pm 1\%$ (2σ). Values are reported in units of per mill relative to Vienna Standard Mean Ocean Water (V-SMOW).

The analytical protocol for S-isotope measurements in pyrite using a CAMECA ims 7f SIMS was similar to that described by Riciputi et al. (1996). Sulfur isotope ratios ($^{34}\text{S}/^{32}\text{S}$) from pyrite were measured using a Cs^+ primary beam and monitoring S^- secondary ions with extreme energy filtering of 200 eV. The ~ 3 -nA primary ion beam was focused to a 15×30 - μm spot using a 100- μm aperture in the primary column. Secondary sulfide ions were detected sequentially by switching the magnetic field. The standard used in this study was Balmat pyrite [$+14.6\%$ Canyon Diablo Troilite (CDT)] from the Balmat mine, New York (Crowe and Vaughan 1996). In general, the overall precision was $\pm 0.4\%$. Sulfur isotopic values are reported in per mill relative to CDT.

Carbon isotope analysis

Carbon-rich material was extracted from the samples using a micro-drill. Carbon-rich powders (0.031 to 1.864 mg) were loaded into tin capsules and combusted using a Costech elemental analyzer. CO_2 gas was introduced into a Thermo Electron Delta V plus gas-source mass spectrometer using a continuous flow system at the University of Manitoba. Calibration was performed by analyzing two international standards (USGS40 and USGS41; L-glutamic acid) at the beginning, middle, and end of each run. A calibration line was calculated by least squares linear regression using the known/recommended and measured isotope values of the calibration standards. To check the quality of analysis, an international graphite standard NBS21 ($\delta^{13}\text{C} = -28.13 \pm 0.03\%$) was analyzed together with unknown samples. Replicate analyses of NBS21 graphite gave a $\delta^{13}\text{C}$ value of $-28.53 \pm 0.08\%$ ($n=6$).

Geochronology

The analytical protocol for U–Pb isotope measurements of uraninite using a CAMECA ims 7f SIMS was similar to that described by Fayek et al. (2002). The TS A uraninite standard was used to correct for IMF, which consists of a single natural uraninite cube (1×1.5 cm) from a pegmatite unite from the Topsham Mine, Maine. Chemical and U–Pb isotopic analyses by SIMS of the grain indicate that it is homogenous, with a near-concordant U–Pb age of 314 ± 10 Ma. The near concordance of and the 314 Ma age of the TS A standard suggests that the U-series isotopes have reached secular equilibrium, assuming that the grain remained closed with respect to its U–Th isotope system. Therefore, this grain was also used as a standard from U-series analysis of very young (<1 Ma) uranium minerals.

Radioactivity measurement

Using highly sensitive radiation home build Oak Ridge National Laboratory counters, the amount of α , β , and γ radiations produced by each sample from DDH PB1 was measured. Samples were placed in each counter for 1 min, and the accumulated radiation was noted. The radiation was plotted versus depth and largely matched the measurements obtained using downhole radiation meters. The greatest amount of radiation ($\sim 1,000$ cps) was measured in sample PB1024009 collected at a depth of 190.8 m.

High-resolution transmission electron microscope

Transmission electron microscope (TEM) samples were prepared from ~ 30 - μm -thick polished thin sections that were analyzed by SIMS. Backscattered electron images were obtained for each sample to locate the exact area analyzed by SIMS. TEM samples of those areas were prepared by drilling 3-mm-diameter disks using an ultrasonic drill. The disks were then mechanically thinned by the tripod method to less than 10 μm . The final “thin film” was produced by bombardment with 4.0 kV Ar^+ ions in a Gatan Precision Ion Polishing System. Analytical electron microscopy and high-resolution TEM analysis were obtained using a JEOL 2010F with a point image resolution of 0.23 nm and an accelerating voltage of 200 kV. In obtaining selected area electron diffraction patterns, we used a constant size selected aperture so that the size distribution of the uraninite micro-domains could be inferred. An Emispec ES vision 4.0 STEM element mapping system was used to obtain bright field scanning TEM distribution maps of Si and U at the nanoscale. The TEM holders were cleaned by plasma (Fischone model C1020) before operation to minimize contamination.

Uranium mineral paragenesis

SEM examination of 40 samples dominantly coming from the seven uranium localities reported in Fig. 2 as well as from the drill core from Nopal I shows the presence of four post-depositional stages of mineral formation (Fig. 4). Stage A minerals are associated with the cooling-related devitrification processes. Stage B minerals precipitated under reducing conditions in fluids ascending through breccia zones and fractures after an intense leaching of the host rock. Stage C minerals result from the action of oxidized meteoric waters, which overprint stage A and stage B assemblages. Stage D minerals formed by precipitation after alteration of stage B and C minerals.

Stage A uraninite is interpreted to have formed from the glassy matrix as this element occurs as U(V) and U(IV) in magmas (Calas 1979) and is easily mobilized as U(VI) during the leaching accompanying glass devitrification as a result of oxidizing conditions and of U(V) disproportionation (Rosholt and Noble 1969; Calas et al. 2008). Relict stage A uraninite is fine-grained (0.1–1 μm), and high-resolution transmission electron microscope (HRTEM) selected area diffraction

and lattice images show it is well crystallized and defect-free (Fig. 5a; Fayek et al. 2002). It is embedded in secondary quartz, which protected it from late hydration or oxidation.

Stage B uraninite (2–30 μm) occurs either as fine intergrowths with stage A uraninite or as fine coatings on stage B pyrite (Figs. 3h, 5b). This pyrite occurs either as framboidal or cubic crystals in the silicified matrix, or as colloform overgrowths lining fractures (Fig. 3f). At the Nopal I deposit, large (10–15 cm) patches of solidified organic matter occur near the top portions of the breccias pipe (Fig. 3d). In 10PB-URAN1, organic-rich zones are surrounded by uranophane and pyrite, also associated to organic matter (Fig. 6a). The organic matter has a stringy appearance (Fig. 6b), while the pyrite grain has a spongy texture (Fig. 6c). Fine-grained uranium minerals (<1 μm) are present in micron-sized cavities that are filled with organic matter, which may have been produced from sulfate-reducing bacteria (Fig. 6d). In PB105c, a stage B pyrite grain is associated with uranophane in a silicified matrix that contains numerous bacterial-shaped features, 1 to 2 μm long and 0.5 μm wide (Fig. 6e–g). These features indicate a carbon-rich material, as indicated by EDS (Fig. 6h). Similar

Phases	Stage A		Stage B	Stage C	Stage D late alteration by descending meteoric fluids
	volcanics deposit	devitrification			
Feldspars					
Quartz			silicification		
Ilmenite					
Anatase			?	ilmenite pseudomorphs	
Uraninite		matrix	associated with pyrite and kaolinite	colloform Urn	late coatings on pyrite
Uranyl silicates					oxidation of uraninite
Uranyl oxy-hydroxydes					oxidation of uraninite
Pyrite			associated with uraninite and kaolinite		
Hematite					oxidation of pyrite
Kaolinite			alteration of feldspars	?	
Jarosite					oxidation of pyrite

Fig. 4 Paragenetic sequence of mineralization from PB-1 Nopal I drill core for the three main stages identified in the petrological study. *Thickness of bars* denotes the relative abundance of the minerals

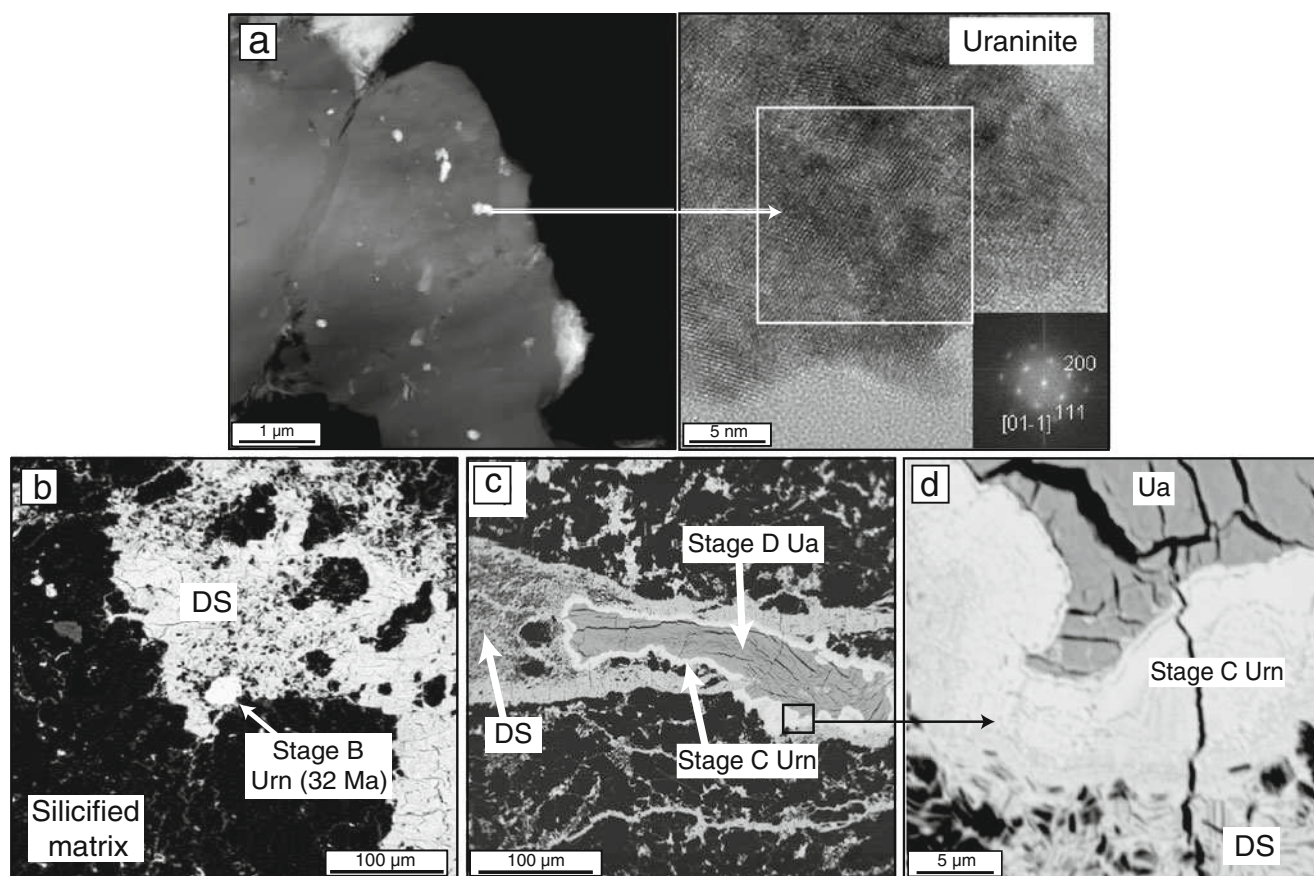


Fig. 5 **a** HRTEM image of primary stage A uraninite showing very few defects exsolved out of the matrix; **b** Backscattered electron image of the central portion of the Nopal I deposit showing textural relationships between 32 Ma stage B uraninite (Urn) and stage C schoepite/dehydrated schoepite; **c** Backscattered electron image of a sample from

the central portion of the Nopal I deposit (upper Nopal fm) showing textural relationships between stage C uranium minerals (*Ua* uranophane); **d** High-magnification image of the area localized in (c) showing the corrosion of stage C colloform uraninite to uranophane

bacterial relicts have been documented in sedimentary pyrite. In the Black Mesa coal deposit in northeastern Arizona (Southam et al. 2001), 2–3- μm -long bacterial-shaped pyrite exhibits a $\delta^{34}\text{S}$ value of -31.7% , which is consistent with the sulfide having a biogenic origin. The presence of this bacterial-shaped pyrite suggests pyritization of microbial colonies under reducing conditions.

Textural evidence indicates that pyrite and stage B uraninite are coeval (Fig. 3i). Paragenetic relationships between uraninite, pyrite, and the silicified host tuff suggest that silicification was synchronous with the fluid event that resulted in the precipitation of stage B minerals. Moreover, uraninite formation is contemporaneous with hydrothermal argillization, which leads to the formation of kaolinite containing radiation-induced defects (Ildefonse et al. 1990; Muller et al. 1990; Calas et al. 2004). Silicification allowed the preservation of stage B pyrite grains from hematitization (Fig. 3i). This silicification event also protected stage B uraninite grains from late oxidation. Preliminary SIMS U–Pb data show that Nopal I stage B uraninite is 32 ± 8 Ma old (Fayek et al. 2006; Fig. 5b).

In Upper Nopal fm, stage C uraninite (which is the most abundant form of uraninite from the Nopal I deposit) is texturally colloform (Fig. 5c) and alters to stage D uranophane from core to rim (Fig. 5d). Stage D U(VI)-minerals (such as α -uranophane $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}$, schoepite $(\text{UO}_2)_8\text{O}_2(\text{OH})_{12} \cdot 12\text{H}_2\text{O}$, dehydrated schoepite $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$, weeksite $\text{K}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 4\text{H}_2\text{O}$, and boltwoodite $\text{K}(\text{UO}_2)(\text{SiO}_3\text{OH}) \cdot 1.5\text{H}_2\text{O}$) are observed as fracture fills and veinlets, as well-developed disseminated crystals, as coatings on large felsic clasts and locally inside the matrix, where they replace feldspars in both Upper Nopal. The Pozos fm, which occurs 90 m below the Nopal I deposit, has high uranium contents (~ 900 ppm; Fig. 3d) where pyrite and anatase (TiO_2) are rimmed and pseudomorphically replaced by stage D uraninite. The reducing environment associated with the Pozos fm created a trap where the dissolved uranium, transported by descending meteoric fluids from the Nopal I deposits, precipitated on the surface of anatase and pyrite.

The lower portions of the Nopal fm (Fig. 3d) are highly oxidized, hematite-rich, and completely devoid of pyrite and

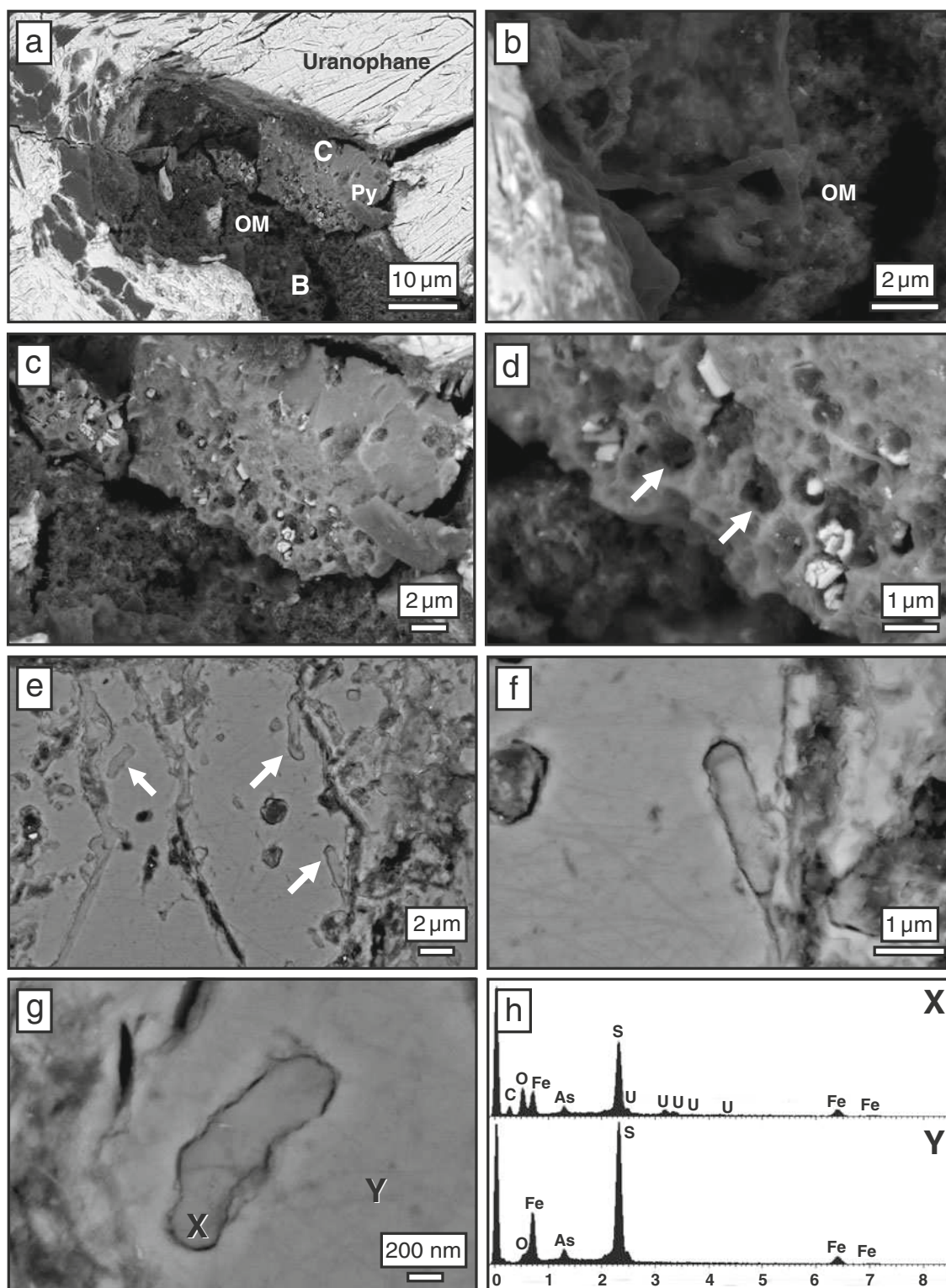


Fig. 6 Scanning electron micrographs of samples 10PB-URAN1 (a–d) and PB105c (e–g) using backscattered electron detector. **a** A zone of organic matter associated with a grain of pyrite (Py) surrounded by uranophane and silicate crystals (left); note the location of micrographs **b** and **c**. **b** High-magnification view of the organic matter showing a stringy texture and the pyrite grains (**c** and **d**) showing a sponge-like texture with organic matter (arrows) infilling ~1-μm-wide cavities, bright spots are uranium minerals. **e** A portion of a pyrite grain

(~0.1 mm long) that shows micron-scale, bacterial-shaped features (arrows) with high-magnification views seen in micrographs **f** and **g**. These features appear as rod-shaped lateral cross sections that are defined by darker outlines, likely carbon-rich material. The EDS data (**h**) show the presence of carbon and uranium in these features (X), which is in contrast to the absence of these elements in the surrounding pyrite (Y)

uranium-rich minerals. The matrix from the lower Nopal fm is more porous and relatively unsilicified compared to the upper portions of the Nopal fm (Dobson et al. 2008). It may therefore have permitted oxidizing fluids from meteoric origin to flow through this level, oxidizing Fe sulfides to hematite, and remobilizing stage A and stage B uraninite (Fig. 4) to form the several generations of stage U(VI)-minerals observed along the drill core and in the Pozos conglomerate (Fig. 5b–d). The mineral paragenesis is summarized in Fig. 4 and corroborates the ages reported by Percy et al. (1994).

Stable isotope geochemistry

Stage B uraninite from Nopal 1 has a $\delta^{18}\text{O} = -10.8\text{‰}$, whereas stage C uraninite within the Pozos conglomerate has a $\delta^{18}\text{O} = -1.5\text{‰}$ (Fayek et al. 2006). If it is assumed that both uraninite generations precipitated from local meteoric water ($\delta^{18}\text{O} = -7\text{‰}$; IAEA/WMO 2006; Calas et al. 2008), then equilibrium temperatures calculated using the uraninite–water fractionation factor equation of Fayek and Kyser (2000) are 45–55°C for stage B uraninite from the ore body and ~20°C for stage C uraninite hosted by the Pozos conglomerate. These temperatures are consistent with the isotopically derived temperature of the hydrothermal alteration events associated with emplacement of uraninite at Nopal I (Calas et al. 2008). In addition, if we use the oxygen isotopic composition of the kaolinite associated with uraninite B

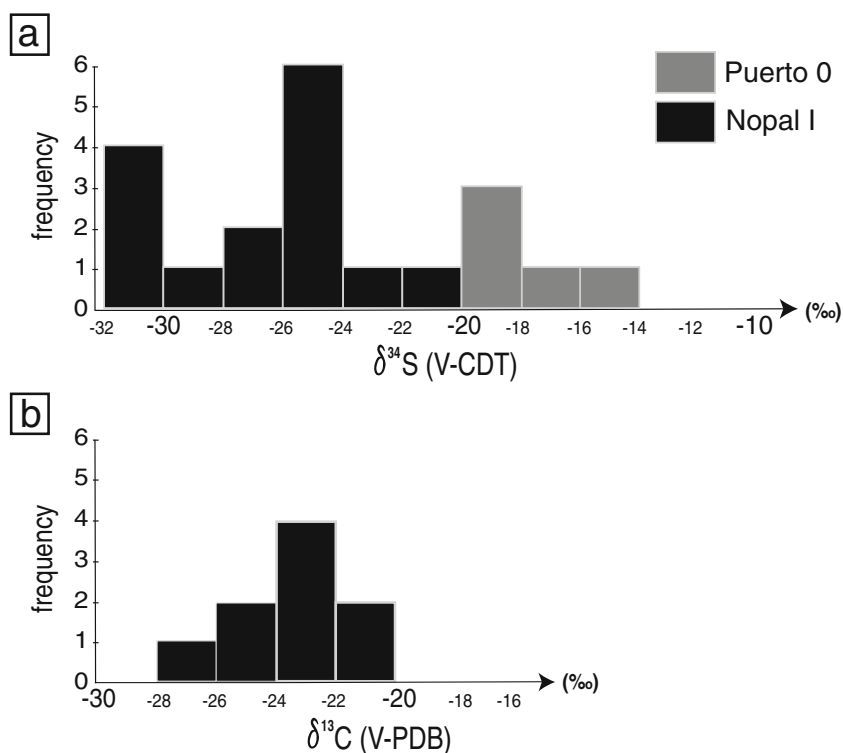
(Calas et al. 2008), kaolinite–water fractionation factor (Sheppard and Gilg 1996), and the uraninite–water fractionation factor (Fayek and Kyser 2000), we again obtain a ~50°C formation temperature for stage B uraninite from the main ore body.

$\delta^{34}\text{S}$ values derived from SIMS analyses of stage B pyrite in Nopal Formation and Pozos Formation along the Nopal I drill core and on a sulfide-rich hand specimen from Puerto 0 mine (locality 6, Fig. 2a) are shown in Fig. 7a. A complete data set is available in Appendix 1. $\delta^{34}\text{S}$ values range between -31.7‰ and -15.7‰ . The lower values (average, -27‰) are from the drill core from Nopal I, whereas the higher values are from Puerto 0 (average -18‰). There is no correlation between texture (cubic crystals, framboidal, and colloidal pyrite/marcasite associations) and the $\delta^{34}\text{S}$ values. The low $\delta^{34}\text{S}$ values indicate a biogenic source for sulfur (see below). The carbon isotopic composition of micro-drilled organic-rich samples from Nopal I, analyzed by continuous flow isotope ratio gas-source mass spectrometry, shows low $\delta^{13}\text{C}$ values, ranging from -27.9‰ to -20.6‰ (Fig. 7b), also an indication of their biogenic origin.

Geochemical implications for the origin of the U mineralization

Such low $\delta^{34}\text{S}$ values are usually associated with the activity of sulfate-reducing bacteria at low temperature within the sedimentary pile (e.g., Blakeman et al. 2002). Indeed,

Fig. 7 **a** $\delta^{34}\text{S}$ values of stage B pyrite from this study, reported in per mil relative to Canyon Diablo Troilite. **b** $\delta^{13}\text{C}$ values of Nopal I carbon-rich patches, reported in per mil relative to PeeDee Belemnite reference



sulfate-reducing bacteria (e.g., *Desulfovibrio desulfuricans*) are known to readily metabolize ^{32}S relative to ^{34}S (Berner 1985; Lovley and Philips 1992; Seal 2006) and therefore enrich in ^{32}S the sulfide phases relative to the sulfates (Berner 1985). In addition, the low $\delta^{13}\text{C}$ values are consistent with $\delta^{13}\text{C}$ values obtained for organic matter from other uranium deposits (e.g., Gauthier-Lafaye and Weber 2003). However, Cretaceous limestone rocks can also be a source of both sulfur and uranium (~2–3 ppm U and 490 ppm S; Stege 1979; Goodell 1985). There are several characteristics of the uranium deposits of the Peña Blanca district that argue against the Cretaceous limestone as the source of the low ^{34}S values and of the uranium concentrations. Firstly, uranium and sulfur transport requires oxidizing fluids, and sulfates generally incorporate ^{34}S rather than ^{32}S (e.g., Rees 1973). Therefore, the observed low $\delta^{34}\text{S}$ values would require a complete oxidation of sedimentary sulfides. However, there is no evidence of extensive leaching and dissolution during fluid circulation in the limestone below the deposits. A second argument is that the volcanic units away from the deposits generally have elevated uranium contents (5–50 ppm; Calas et al. 2008). Altered volcanic rocks show a broad redistribution of U, with evidence of leaching associated in the breccia zones (Fig. 3a; 4 ppm; Calas et al. 2008) as the uranium content of the Cretaceous basement limestone remains uniform. Finally, separate fluids would be required to transport sedimentary sulfur as ^{32}S -rich HS^- or H_2S and uranium as U(VI) , in reducing and oxidizing conditions, respectively. This seems unlikely.

Uranium ore deposits associated to biological activity have been widely documented, with associated sulfides showing low $\delta^{34}\text{S}$ values (~–20‰). However, most examples concern sedimentary ore deposits, such as sandstone-hosted roll-front uranium deposits (Northrop and Goldhaber 1990; Min et al. 2005; Cai et al. 2007). By contrast, $\delta^{34}\text{S}$ values of hydrothermal sulfides associated with uranium deposits generally range from –6 to +10‰ (Fayek and Kyser 1999). Microbial activity associated with uranium deposits from the Peña Blanca district suggests that pyrite precipitated below 140°C (Suzuki and Banfield 1999). Precipitation of uraninite from low-temperature (~50°C) fluids at the Nopal I deposit correlates with the calculated oxygen isotope temperature estimates. In addition, the uraninite is also associated with organic-rich patches that have low $\delta^{13}\text{C}$ values, which suggests that these organic patches have a microbial origin and confirms an intense biological activity during uraninite and sulfide precipitation.

Genetic model

Our data indicate that the uranium deposits of the Peña Blanca district result from an intense biological activity

developed in low-temperature geothermal, meteoric fluids, focused in well-defined tectonic breccia zones located at the intersection of two or more fault systems (Fig. 8a). Periods of low tectonic activity were accompanied by filling and cementation of these brecciated zones. Episodic reactivation of these faults resulted in focused fluid flow along the most brecciated localities. As shown by O- and H-isotope geochemistry, geothermal fluids were of meteoric origin (Calas et al. 2008). Heating of ground waters by a local magmatic source is suggested by the presence of the stage 1 dykes. Although no plutonic rocks are reported in the studied area, the emplacement of a deeper magmatic body may have been facilitated by the presence of the NW–SE (stage 4) fault network linked to the activity of the Caltam lineament (Fig. 1, inset). Ascending oxidized meteoritic fluids altered the ignimbrites resulting in mobilization of uranium from the glassy matrix of the volcanic rocks. The precipitation of stage B kaolinite, pyrite, and uraninite indicates reducing conditions (Fig. 8a). Low $\delta^{34}\text{S}$ values of the sulfides and presence of patches of microbial origin support the presence of sulfur-reducing bacteria, associated with low-temperature fluids, not only along the faults but also in fractures and voids in the vicinity of the main ore deposits. The age of this uraninite, 32 ± 8 Ma (Fayek et al. 2006), corresponds to early Basin and Range tectonics and to an active period of the long-lived Sierra Madre Occidental magmatic activity (Bryan et al. 2008).

Subsequent tectono-magmatic activity resulted in structural reactivation of the fault and fracture networks (Fig. 8b). The fluids associated with this activity overprinted stage B minerals and locally remobilized uranium. However, a detailed chronology of late-stage fluid circulation events remains poorly constrained because of brecciation and associated fluid flow that extensively overprinted earlier stage A and B paragenesis. Reactivation of fault networks and remobilization of uranium-rich phases locally led to the precipitation of stage C uraninite (Fig. 5c, d) within Nopal fm. This uraninite generation corresponds to the “colloform uraninite” reported by Percy et al. (1994), which gave a chemical Pb age of 7.9 ± 5.2 Ma, which is similar to the U–Pb isotopic ages for uraninite obtained by Fayek et al. (2006) and Saucedo (2011). Late fracturing (along Basin and Range and RGR networks) and infiltration of descending meteoric oxidizing waters promoted in turn the alteration of stage B and C uraninite to U(VI) minerals and permitted the formation of stage D uraninite rims around pyrite within Pozos fm. The complex uranium mineralogy of the Nopal 1 deposit is apparently the integrated result of a rather protracted fluid history that includes multiple episodes of mineralization and subsequent alteration, varying from reducing to oxidizing conditions. A change in redox conditions may result from paleoclimatic events (e.g., dry vs. wet periods) or modifications in the microbial reducing activity.

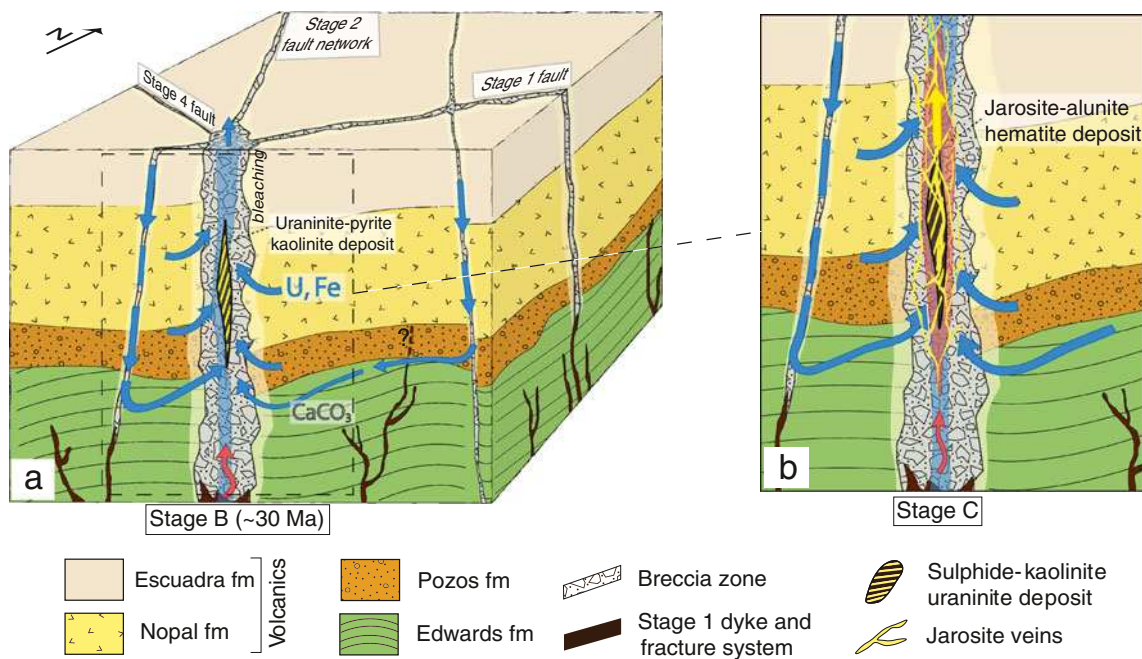


Fig. 8 **a** Idealized sketch of a geothermal vent showing the formation of stage B uraninite–pyrite–kaolinite deposits at the intersection of several fault systems by leaching out the groundmass in the vicinity of the tectonic breccia zone, enriching pervasive groundwater meteoric fluids in U, Fe, and CaCO₃. Uncertainty about vertical extent of dykes within Pozos conglomerate is represented by the question mark. The

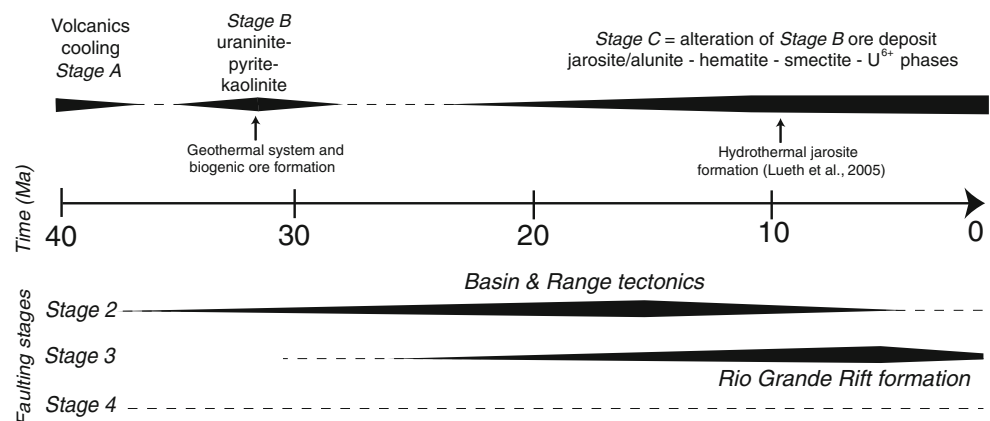
red arrow represents heating of ground waters by a possible heat source associated with a 32-Ma-old magmatic event leading to the formation of this geothermal system. **b** A cross-section showing the alteration of stage B deposits by subsequent oxidizing fluid circulation associated with jarosite–alunite precipitation

The presence of sulfate minerals such as jarosite and alunite suggests that intense oxidizing fluids circulated during late brecciation (Fig. 3h). However, across the Peña Blanca district, multiple generations of jarosite formed from different fluid events. The first fluid event is related to low T (~50°C) processes and affects the whole mining district (colloform jarosite in Nopal I: Prikryl et al. 1997). The second jarosite event might be related to a higher temperature (~150°C) fluid, flowing along hydraulic fractures associated to the main Basin and Range fault that cuts across Las Margaritas (Fig. 3f). This fluid may be related to the 9.4-Ma-old event that precipitated jarosite at Las Margaritas, which (Goodell et al. 1999; Lueth et

al. 2005) formed at 120–225°C, and precipitated Mo, As, Cs, and F mineralizations (Calas 1977; Goodell 1981; Wenrich et al. 1982). The third generation of jarosite formed from supergene processes and is related to alteration and remobilization of former jarosite by late fluid circulation in the most brecciated zones.

New volcanic-hosted uranium ore deposits have been recently found in the nearby San Marcos uranium district (Reyes-Cortés et al. 2010) (Fig. 1). As in the Peña Blanca district, the San Marcos district shows a middle to late Cenozoic extension (Aranda-Gomez et al. 2005) and is located on the western prolongation of the Caltam lineament

Fig. 9 Chronological synthesis of tectonic and mineralogical events affecting the Peña Blanca District. Peaks of tectonic activities and associated fault networks are represented by thick black lines. Low or inferred activities are shown by dotted lines



(Tardy et al. 1989). The deposits present petrological and structural patterns strikingly similar to the deposits here described. Future studies are needed to show the presence of large caldera systems with extensive hydrothermal alteration, including the significance of the microbial activity on uranium mobility and concentration.

Conclusions

The chronology of events affecting the Sierra Peña Blanca uranium deposits is summarized in Fig. 9. Four important geologic events affected the Peña Blanca uranium district. These are associated with post-Cretaceous emplacement of felsic dykes, Basin and Range tectonics, Rio Grande rifting, and reactivation of Caltam lineament. The tectonic control on the mineralization is illustrated by the association of the uranium deposits with brecciated zones, at the intersection of two or more fault networks, periodically reactivated during late Cenozoic tectonic events. This may be associated with magmatic pulses.

A major finding of this study is the evidence for a microbial origin of U mineralization and associated sulfides and organic matter. Biological activity indicates possible mechanisms for reducing the epithermal oxidizing fluids, which resulted in the formation of the uranium deposits in the Peña Blanca district. The oxidizing fluids were efficient at mobilizing uranium contained in the volcanic felsic glass, which is a major local source of uranium. Together with previous $\delta^{18}\text{O}$ and δD data from associated clay minerals, the $\delta^{18}\text{O}$ data obtained from uraninite are consistent with low-temperature (between 50°C and 75°C) epithermal fluids. The redox conditions were mainly controlled by biological activity and show the importance of microorganisms in the formation of these unusual epithermal deposits.

Acknowledgments The authors thank A.L. Saucedo (University of Manitoba), P. Goodell (University of Texas, El Paso), I. Reyes-Cortes, and R. de la Garza (Facultad de Ingeniería, Universidad Autónoma de Chihuahua) for fruitful discussions, comments, and assistance on the field. We are also indebted to Manuel Pubellier, David Thomas, and Virgil Lueth for valuable comments on the manuscript. This work was partially funded by an NSERC Discovery and CFI Grant to Fayek and the Canada Research Chair program. This manuscript greatly benefited from the thorough reviews by Dr. Aleshyn and Associate Editor Michel Cuney and comments by the Editor Bernd Lehmann.

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