

U redox fronts and kaolinisation in basement-hosted unconformity-related U ores of the Athabasca Basin (Canada): late U remobilisation by meteoric fluids

Julien Mercadier · Michel Cuney · Michel Cathelineau · Mathieu Lacorde

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Abstract Proterozoic basement-hosted unconformity-related uranium deposits of the Athabasca Basin (Saskatchewan, Canada) were affected by significant uranium redistribution along oxidation–reduction redox fronts related to cold and late meteoric fluid infiltration. These redox fronts exhibit the same mineralogical and geochemical features as the well-studied uranium roll-front deposits in siliclastic rocks. The primary hydrothermal uranium mineralisation (1.6–1.3 Ga) of basement-hosted deposits is strongly reworked to new disseminated ores comprising three distinctly coloured zones: a white-green zone corresponding to the previous clay-rich alteration halo contemporaneous with hydrothermal ores, a uranium front corresponding to the uranium deposition zone of the redox front (brownish zone, rich in goethite) and a hematite-rich red zone marking the front progression. The three zones directly reflect the mineralogical zonation related to uranium oxides (pitchblende), sulphides, iron minerals (hematite and goethite) and alumino-phosphate-sulphate (APS) minerals. The zoning can be explained by processes of dissolution–precipitation along a redox interface and was produced by the infiltration of cold (<50°C) meteoric fluids to the hydrothermally altered areas. U, Fe, Ca, Pb, S, REE, V, Y, W, Mo and Se were the main mobile elements in this process, and their distribution within the three zones was, for most of them, directly dependent on their redox potential. The elements concentrated in the redox fronts were sourced by the alteration of previously crystallised

hydrothermal minerals, such as uranium oxides and light rare earth element (LREE)-rich APS. The uranium oxides from the redox front are characterised by LREE-enriched patterns, which differ from those of unconformity-related ores and clearly demonstrate their distinct conditions of formation. Uranium redox front formation is thought to be linked to fluid circulation episodes initiated during the 400–300 Ma period during uplift and erosion of the Athabasca Basin when it was near the Equator and to have been still active during the last million years. A major kaolinisation event was caused by changes in the fluid circulation regime, reworking the primary uranium redox fronts and causing the redistribution of elements originally concentrated in the uranium-enriched meteoric-related redox fronts.

Keywords Redox · Front · Uranium · Athabasca · Canada · Remobilisation · Meteoric · Kaolinite

Introduction

U deposits associated with the Athabasca Basin (Saskatchewan, Canada) are classified as unconformity-related deposits and located in the sedimentary basin or in the subjacent basement rocks. They are considered to have been formed by hydrothermal fluid circulations between 1.3 and 1.6 Ga (Cumming and Krstic 1992; Fayek et al. 2002a, b; Jefferson et al. 2007; Alexandre et al. 2009). In this model, the fluid responsible for the U uptake and transport is an oxidising diagenetic brine present in the basal sandstone of the basin (Pagel 1975), probably expelled from evaporitic layers (Derome et al. 2005; Richard et al. 2010) which percolated into the basement and created clay-rich alteration haloes related to U deposition. The temperature of the fluids that precipitated the primary ores was

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J. Mercadier (✉) · M. Cuney · M. Cathelineau · M. Lacorde
G2R, Nancy-Université, CNRS, CREGU,
Boulevard des Aiguillettes, B.P. 239,
54506 Vandœuvre lès Nancy, France
e-mail: julien.mercadier@g2r.uhp-nancy.fr

estimated from fluid inclusion microthermometry and ranges from 130°C to 220°C, assuming a depth of around 5 km for the pressure correction (Pagel 1975; Derome et al. 2005).

Oxygen and hydrogen isotopic analyses of alteration haloes, and especially kaolinite-rich zones, around U mineralisation have highlighted massive circulations of a late and low-temperature meteoric fluid (Halter et al. 1987; Wilson and Kyser 1987; Kotzer and Kyser 1995). This episode was principally thought to be associated with kaolinite formation replacing the illite- and chlorite-rich hydrothermal alteration matrix, close to the major tectonic structures. The circulations have been postulated to have been Post-Cretaceous and related to the final uplift of the Athabasca Basin (Hoeve and Quirt 1984). Furthermore, it has been proposed to have caused a strong remobilisation of the uranium and a substantial loss of radiogenic Pb (Quirt 1989; Kister et al. 2004). Nevertheless, the majority of the previous studies on unconformity-related deposits have focussed on the conditions of primary ore genesis by studying the best preserved hydrothermal mineralisation. No previous mineralogical and geochemical work has been carried out on the remobilisation features or assessed their impact on the current distribution of U ore in the unconformity-related deposits.

Here, we present the first detailed study of the late meteoric-related U redox fronts in two basement-hosted U deposits of the Athabasca Basin, namely Eagle Point and P-Patch. In both deposits, the primary U ore bodies were strongly remobilised within the clay-rich alteration halo (Fig. 1). At the outcrop scale, the resulting mineralisation exhibits strong similarities with roll-front U deposits described in sedimentary host rocks (Fischer 1950; Shawe and Granger 1965; Adler 1974; Harshman 1974 among others), or in granite-hosted deposits (Cathelineau 1982), and is characterised by a typical colour zoning from red to brownish and white-green. At Eagle Point and P-Patch deposits, redox front U ores have a lower grade than the primary ore, but may represent more than 80% of the U resource, as observed by the authors during systematic logging of the P-Patch deposit or during the visit of the 02 North Extension site in the Eagle Point mine.

The purpose of this study was to understand the origin and the meaning of the late U redox fronts from petrographic, geochemical, geochronological and mineralogical studies and to determine the timing and conditions of their formation and their relationships to both hydrothermal U concentrations and to meteoric-related kaolinite-rich zones. The results are compared to those from the literature on sedimentary-hosted U roll-front deposits to estimate the physicochemical conditions of U redox front formation in the basement of the Athabasca Basin and to propose a genetic model for these well-developed but still poorly studied U occurrences.

Geological setting

Geology of the Athabasca Basin

The basement of the Athabasca Basin comprises mainly of Archean tonalitic to granitic domes surrounded by Paleoproterozoic (Aphebian) metasedimentary rocks and Late Paleoproterozoic (Hudsonian) mafic to felsic plutons (Madore et al. 1999; Thomas et al. 2000; Annesley et al. 2005 among others). Two distinct structural provinces are distinguished, namely the Hearne Province to the east and the Rae Province to the west (Fig. 2). In the eastern part of the Athabasca Basin, where most of the known unconformity-type U deposits are located, the basement consists of an assemblage of Archean plutonic rocks and Paleoproterozoic metasediments deposited in an epicontinental setting and belonging to the Wollaston Domain of the Hearne Province. These rocks were affected by polyphase deformation and high-grade metamorphism associated with partial melting and injection of plutonic rocks during the Hudsonian Orogeny at ca. 1860–1720 Ma (Chiarenzelli et al. 1998; Thomas et al. 2000; Annesley et al. 2001, 2005). Maximum P – T conditions at the peak of the Hudsonian Orogeny, between 1840 and 1800 Ma, reached about 800°C and 800 MPa (Annesley et al. 2005). The exhumation of the basement started at about 1814 Ma (peak P – T conditions), the P – T conditions following a retrograde P – T path to pressures of 200–250 MPa and temperatures of 500–550°C at about 1720 Ma (Annesley et al. 2005).

The Athabasca sedimentary basin consists of Late Paleoproterozoic to Early Neoproterozoic (Helikian) polycyclic, mature fluvial to marine quartz-rich sandstone of the Athabasca Group deposited in a nearshore shallow shelf environment (Ramaekers 1990; Fayek and Kyser 1997; Ramaekers et al. 2007), with deposition beginning at about 1700–1750 Ma (Armstrong and Ramaekers 1985; Kotzer et al. 1992; Kyser et al. 2000). The estimated thickness of the basin during Middle Proterozoic times was deduced to have been 5–6 km from fluid inclusion studies (Pagel 1975). The Athabasca Group was cut by several northwest-trending mafic dykes, the MacKenzie dolerite dykes, linked to extension associated with Hudsonian faults (Cumming and Krstic 1992) at 1267 ± 2 Ma (LeCheminant and Heaman 1989).

Deposit geology

The P-Patch U deposit is located in the southeastern part of the Athabasca Basin, 3 km east of the former Key Lake U mine (Fig. 2a). The preserved sedimentary Athabasca Group is 70 m thick above the P-Patch deposit and directly overlies the basement lithologies of the Wollaston Domain. At P-Patch, the Wollaston Domain mainly comprises metasedimentary and pegmatoid/granitoid rocks (Fig. 2a).

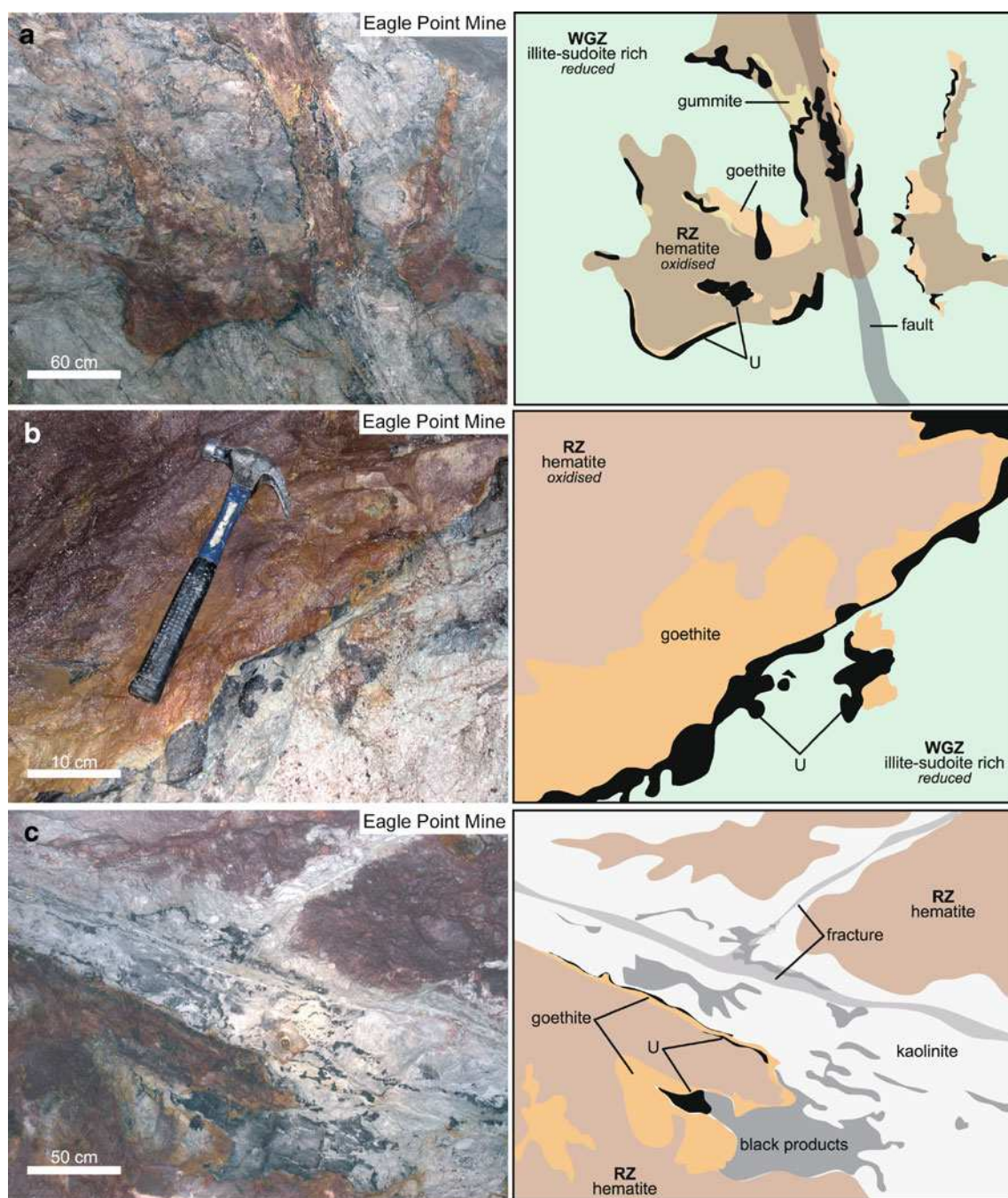


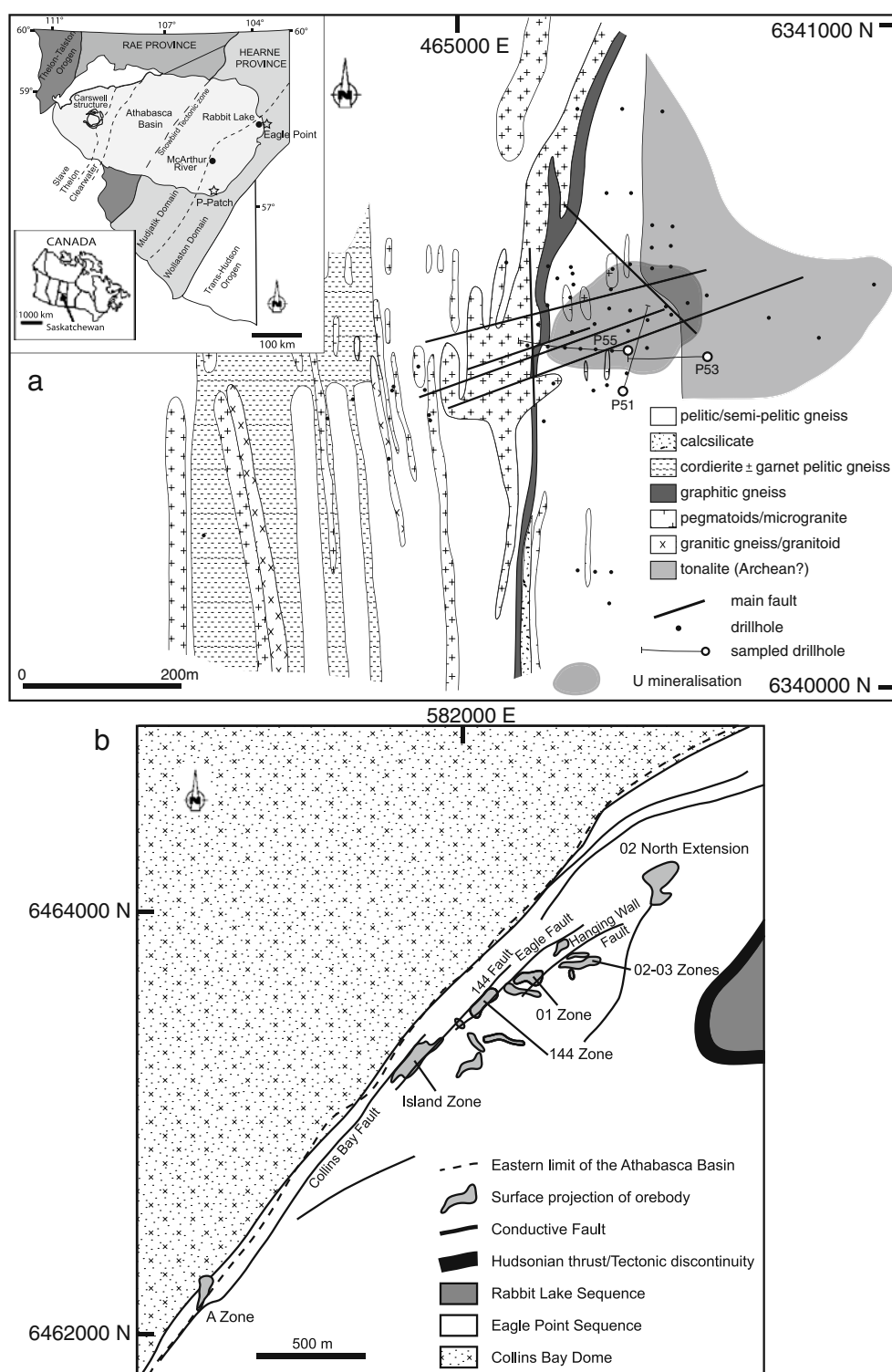
Fig. 1 Photographs and simplified sketches of uranium roll-fronts and kaolinisation in the Eagle Point mine. **a** Typical uranium redox fronts observed with hematite-rich oxidised red zone (RZ), goethite-rich uranium front (U). The redox fronts are closely associated with fluid pathways (*fault*) and develop in the previously altered, reduced white-green zone (WGZ) due to higher porosity and permeability. Recent weathering hexavalent uranium minerals (*gummite*) are visible. **b**

Close-up of a typical uranium redox front in the Eagle Point mine with hematite-rich oxidised red zone (RZ), goethite-rich uranium front (U) and the previously altered reduced white-green zone (WGZ). **c** Redox front crosscut by massive kaolinisation closely associated with a fracture. Uranium, previously concentrated in uranium front (U), is partially redeposited as sooty pitchblende in the kaolinite-rich matrix (*black products*)

Archean granitic gneisses and tonalite domes are present east of the P-Patch deposit and are overlain by Early Proterozoic pelitic to semi-pelitic gneisses, which generally strike to the north and dip 30–60° to the east. A concordant band of graphitic gneiss occurs in the gneiss series in the

central part of the deposit. Cordierite-bearing pelitic gneisses and calc-silicates are minor lithologies in the drilled area. Pegmatoid sills, microgranites and migmatites, derived from the Late Hudsonian partial melting of the metasediments, have intruded as tens of centimetres- to tens

Fig. 2 **a** Simplified geological map of the P-Patch uranium deposit (courtesy of AREVA Resources Inc.). The locations of the sampled drill holes are indicated with their number and orientation. **b** Simplified geological map of the Eagle Point uranium mine. The location of the different uranium occurrences is indicated. The studied samples come from 02 zone and 02 North Extension



of metres-thick lenses that are concordant to slightly discordant with the foliation of the gneisses. A 10- to 30-m-thick regolithic alteration, composed mainly of hematite, chlorite and kaolinite, is developed at the top of the basement. In the P-Patch deposit, N0°E-, N70°E- and N150°E-trending faults have been observed in decreasing

order of abundance. These are largely considered to be related to the reactivation of Hudsonian faults in the basement during basin extension (Mercadier et al. 2010). The primary U ores in the P-Patch deposit are contemporaneous with other unconformity-type mineralisation at the Key Lake mine (Höndorf et al. 1985; Carl et al. 1992;

Kotzer and Kyser 1993) and associated with N70°E-trending dravite–quartz breccias, a direction similar to that of the major Key Lake Fault which hosts the Key Lake pits and several U ore pods (e.g. GAX and BV zones). The stress field during the mineralisation stage was oriented N130°E to N150°E (Mercadier et al. 2010) and has partly reopened structures developed during the Hudsonian retrograde metamorphic stage (ca. 1795–1720 Ma). The complex alteration halo associated with the P-Patch deposit (up to several metres wide) is mainly developed in basement lithologies and characterised by an illite, sudoite (di-trioctahedral Al–Mg chlorite) and dravite (Mg-rich tourmaline) assemblage. Macroscopically, the transition between fresh to altered lithologies can be very abrupt. An assemblage of hydrothermal quartz, dolomite, sudoite and minor sulphides (mostly pyrite) is associated with the primary mineralisation. This assemblage is considered to be contemporaneous with the oldest U ore deposition stage, as in other unconformity-type U deposits from the Athabasca Basin (Jefferson et al. 2007). No clear evidence of a distinct spatial distribution of illite and chlorite alteration is observable around the P-Patch deposit, contrary to the pattern observed in most other Athabasca Basin deposits (Quirt 1989). In the sandstone overlying the P-Patch deposit, an illite alteration associated with some quartz dissolution overprints the regional dickite–kaolinite alteration. This alteration is, however, more discrete than in other unconformity-located U deposits from the Athabasca Basin, such as those at Cigar Lake and McArthur River, and less intense than that in the basement. The ore zone is entirely hosted within basement rocks with no U occurrences at the unconformity. The ore body is small (approximately 200 m long by 200 m wide, with a vertical extension up to 100 m) and plunges to the east (Fig. 2a). Some minor mineralised pods also occur outside this main body. The oldest mineralisation consists of uraninite–pitchblende crystals within a N70°E-trending dravite–euhehedral quartz breccia, located about 100 m below the unconformity. However, the main U stock is represented by a U redistribution close to redox fronts associated with hematite, kaolinite and minor coffinite within reactivated faults and permeable hydrothermally altered rocks. No direct spatial relation between uranium and any graphitic lithology has been observed at P-Patch.

The Eagle Point deposit belongs to a series of basement-hosted U ore bodies along the N45°E Collins Bay reverse fault at the eastern margin of Athabasca Basin (Fig. 2b). The Collins Bay fault is developed in graphitic gneisses of the Wollaston Group at the contact with the Archean granitoids of the Collins Bay Dome. The Wollaston Group is mainly composed of Paleoproterozoic (Aphebian) amphibolites, pelitic to semi-pelitic gneisses, graphitic pelitic gneisses, granitoids and pegmatoids. Athabasca

Basin sandstone is only preserved to the west of the Collins Bay reverse fault. The Eagle Point deposit is structurally controlled by Riedel-type structures along the Collins Bay fault (Renaud 2006). Some smaller U ore bodies in this deposit (01, 02, 03 and 02 North Extension Zones) occur along secondary structures striking N80°E, mostly in the northern part of the deposit. Alteration features closely associated with U mineralised structures are mostly represented by the formation of an illite–chlorite $\pm$ dravite assemblage in the metasediments together with more localised pyritization and carbonate and/or quartz veining. Illite is the dominant clay mineral within the altered and mineralised zones, whilst sudoite is more peripheral (Quirt 1989). Kaolinite and hematite are observed close to the largest structures and have been interpreted to be related to late meteoric fluid circulation (Quirt 1989; Kotzer and Kyser 1995). As reported by Thomas (2003), the main mineralisation is monometallic, consisting of uraninite/pitchblende variably altered to coffinite and occurs in foliation opening, or in fracture- and breccia-controlled veins. It tends to be concentrated in areas where dilational structures are well developed in all rock types. U/Pb ages from Collins Bay zone ore samples give upper intercepts at 1379 ± 6 Ma and 1342 ± 6 Ma by fixing the lower intercept at 573 ± 7 Ma (Cumming and Krstic 1992).

Methodology

Seven samples of meteoric-related redox front U mineralisation were selected from boreholes P51, P53 and P55 at the P-Patch deposit and from borehole DDH 1935 and the 02 Next Extension mine site of the Eagle Point deposit (Fig. 2). The samples selected are characterised by three distinct zones (Fig. 3):

- A reduced white-green zone mainly consisting of an illite–chlorite $\pm$ dravite paragenesis (white-green zone, WGZ);
- A brownish zone representing the U mineralised redox front (uranium front, UF); and
- An oxidised red zone, rich in hematite (red zone, RZ).

In addition, one sample of a kaolinite-rich zone crosscutting a redox front was selected (sample 90-16) from the 02 Next Extension mine site. The characteristics of all the samples are given in Table 1.

Polished thin sections were studied to establish the mineral paragenesis using a conventional transmitted and reflected light microscope, as well as both a PHILIPS XL30 scanning electron microscope equipped with an energy-dispersive spectrometer using a Si(Li) semiconductor detector and a HITACHI S-4800 scanning electron microscope at SCMEM (Nancy, France).

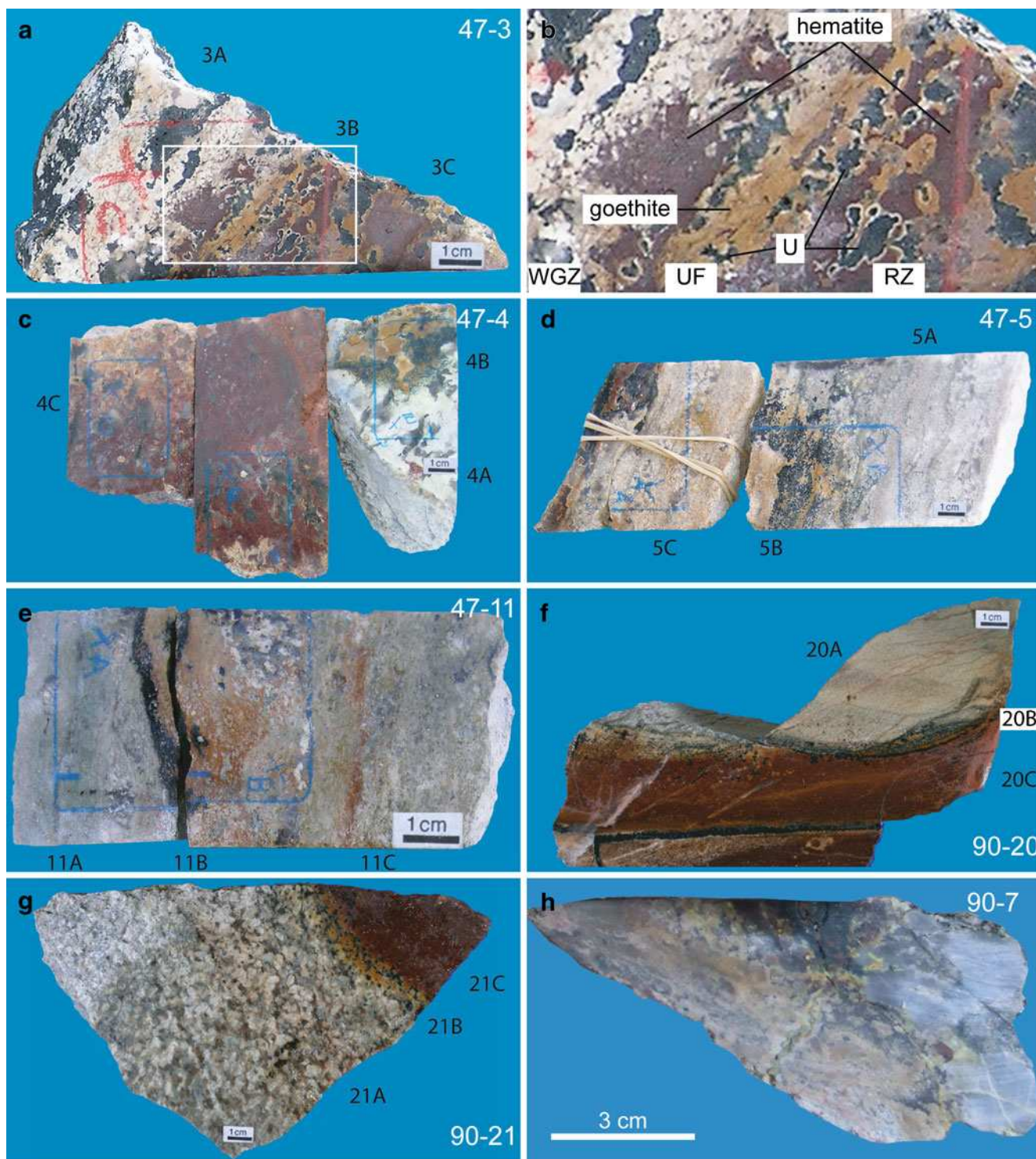


Fig. 3 Photographs of the eight studied uranium redox fronts. The redox front is composed of three zones distinguishable by their colour: a white-green zone (*WGZ*), an orange uranium-rich zone with goethite

(*UF*) and a hematite-rich red zone (*RZ*). The three zones are discriminated using a letter (*A* for *WGZ*, *B* for *UF* or *C* for *RZ*)

Electron microprobe analysis of pitchblende, coffinite and aluminium–phosphate–sulphates (APS) were performed using a CAMECA SX100 microprobe at SCMEM. For pitchblende and coffinite analysis, the calibration used

natural and synthetic oxides or alloys (orthoclase, albite, MnTiO_3 , LaPO_4 , CePO_4 , wollastonite, UO_2 , ThO_2 , PbCrO_4 , SrS , ZrO_2 , hematite, NdPO_4 , YPO_4 , olivine, DyRu_2Ge_2 , V and PbSe). The analytical conditions were:

Table 1 List of the studied uranium redox front samples from P-Patch and Eagle Point deposits

Sample	Deposit	Drill hole	Depth (m)	Unconformity depth (m)	Initial lithology
47-3	P-Patch	P51	218.3	92	Pegmatoid
47-4	P-Patch	P51	241.3	92	Pegmatoid
47-5	P-Patch	P53	230.4	97.3	Pelitic gneiss
47-11	P-Patch	P55	182.6	94.6	Pelitic gneiss
90-7	Eagle Point	DDH 1935	92.2	No sandstone	Pelitic gneiss
90-20	Eagle Point	02 NE	Unknown	No sandstone	Pegmatoid
90-21	Eagle Point	02 NE	Unknown	No sandstone	Pegmatoid
90-16	Eagle Point	02 NE	Unknown	No sandstone	Pegmatoid

02 NE 02 north extension of Eagle Point mine

10-nA current, accelerating voltage of 15 kV, 10-s counting time (K, Na, Ca, S), 20 s (Ti, Ce, U, Th, Zr, Si, Al, Fe, Mn, Y, V, Se), 40 s (P, Mg, Dy, Nd), 50 s for Pb and 60 s for La. When analysed, Mn, La, Ce, Dy, Th, Ta and Se were below the detection limit for pitchblende and coffinite in all the samples (detection limits (in wt.%): Mn=0.28, La=0.13, Ce=0.29, Dy=0.58, Th=0.1, Ta=0.3, Se=0.3). For APS analysis, the calibration used natural and synthetic oxides or alloys (flap, chloroapatite, orthoclase, albite, LaPO_4 , CePO_4 , PrPO_4 , NdPO_4 , SmPO_4 , ThO_2 , UO_2 and SrSO_4). The analytical conditions were similar to U-rich minerals, except for counting times of 10 s for S, 15 s for Sr, 20 s (P, Si, Al, Ca, Th), 30 s for F, 40 s (La, Pr, Nd, U) and 60 s for Ce and Sm. Pb was below the detection limit for APS analysis (Pb detection limit=0.12 wt.%).

Major and trace elements compositions for whole rock analysis were obtained by chemistry, ICP-OES and ICP-MS spectrometry (LiBO_2 fusion, Carignan et al. 2001) at the SARM laboratory, CRPG (Nancy, France). The three zones (RZ, UF and WGZ) of six samples (47-3, 47-4, 47-5, 47-11, 90-20 and 90-21) were individually analysed.

Chemical ages for U oxides and whole rock geochemistry were calculated from the following equation of Bowles (1990) modified by Kister (2003):

$$\text{Pb} = \text{Th} \times \frac{208}{232} \times (e^{\lambda_{232}t} - 1) + \text{U} \times \left(206 \times \frac{0.9928}{238.04} \times (e^{\lambda_{238}t} - 1) + 207 \times \frac{0.0072}{235} \times (e^{\lambda_{235}t} - 1) \right)$$

where t is the age of U deposition, λ_{232} , λ_{235} and λ_{238} are the decay constants of ^{232}Th , ^{235}U and ^{238}U , respectively, and Pb, Th and U are the weight percent fractions of these elements in the analysed U mineral or in whole rock. The formula is based on the assumption that no U has been reintroduced into or lost from the system and that no common lead was present in the system during the initial crystallisation. The calculation initially proposed by Bowles (1990) for minerals was applied to the whole rock U, Th

and Pb contents to compare the obtained age to the chemical and/or isotopic ages determined on uranium oxides. Both calculated chemical ages need to be interpreted with caution, but data were, however, used to evaluate the coherence of the lead contents in rock with those expected if one of the two uranium mineralisation types, primary or secondary, predominates. If the two chemical ages are similar, lead in the rock as to be considered as totally controlled by redox front uranium oxide. The origin of the lead (from alteration of unconformity-related mineralisations or linked to redox front) can be constrained in the different parts of the redox front (WGZ, UF and RZ) by this method.

U/Pb isotopic compositions of U oxides were measured with a CAMECA IMS 3f ion microprobe at the CRPG (Nancy, France). A 10-kV O^- primary beam of 5- to 10-nA intensity was focussed to a spot of 30 μm in diameter. Secondary ions were accelerated to 4,500 eV and analysed at a mass resolution of 800% with an energy filtering at -80 ± 20 V. Nine different atomic masses ($^{203.5}\text{Pb}$, ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th , ^{238}U , ^{248}ThO and ^{254}UO) were measured by peak switching, with counting times of 4 s, except for ^{204}Pb (8 s), and a waiting time of 1 s. Positive secondary ions were counted on an ion multiplier on an ion counting mode, with a dead time of 22 ns. Sixty successive measurement cycles were accumulated for 50 min on each sample position. The energy offset allows the removal of complex molecular interferences and stabilises the U/Pb relative ionisation yield. The $^{235}\text{U}/^{206}\text{Pb}$ ratios were calculated using a $^{238}\text{U}/^{235}\text{U}$ value of 137.88 and the measured $^{238}\text{U}/^{206}\text{Pb}$ ratio. During the measurement process, a mass-dependent bias (instrumental mass fractionation) was introduced to favour the light isotope (Shimizu and Hart 1981). The fractionation of Pb isotopes was <1% (Deloule et al. 1986). Common Pb corrections were based on the measured ^{204}Pb content using the Pb isotopic composition calculated from Stacey and Kramers (1975), at the age of the uraninite. However, the high $^{206}\text{Pb}/^{204}\text{Pb}$ ratio (>10,000) obtained for all samples suggests that there

is negligible common lead. The standard utilised for U/Pb isotopic analysis was a uraninite from Zambia (Holliger 1988), which has a given concordant age at 540 ± 4 Ma (Cathelineau et al. 1990). Ages and error correlations were calculated using the ISOPLOT flowsheet of Ludwig (1999). Uncertainties in the ages are reported at the 2σ level.

Rare earth element (REE) concentrations in pitchblende were measured with a CAMECA IMS 3f ion microprobe at the CRPG for sample 90-7 and with a CAMECA IMS 7f ion microprobe at CEA (Bruyères le Chatel, France) for samples 47-3 and 90-20. The methodology and calibration of SIMS analysis for rare earth element determination is described in Bonhoure et al. (2007) for CAMECA IMS 3f and in Piani et al. (2008) for CAMECA IMS 7f. The REE standard for both ion microprobes was a uraninite from the Mistamisk Valley, Canada (Kish and Cuney 1981). Gd and Yb cannot be directly measured using the methodology of Bonhoure et al. (2007) due to isotopic interference with several light rare earth element (LREE) oxides (LaO, CeO, PrO and NdO particularly for Gd) and were therefore interpolated. The relative abundances reported for the two elements in this study were calculated taking into account the relative abundances of neighbouring REE. For example, to calculate Yb relative abundance, measured Lu and Tm relative abundances were used: $Yb = 0.5 \times (Tm) + 0.5 \times (Lu)$. In the case of Gd, anomalous Eu was replaced by Sm relative abundance in the calculation: $Gd = 1/3 \times (Sm) + 2/3 \times (Tb)$. The calculation methodology was tested using the values obtained for these two elements using the CAMECA IMS 7f in microprobe on the standard.

The presence of hematite and goethite in the U front and the red zone were confirmed using a Dilor-Labram Raman microspectrometer at G2R laboratory equipped with an ionised argon laser (2020, Spectraphysics; wavelength 514.532 nm), the determination between both species being realised using specific bands of each minerals (247, 298, 390, 485 and 553 cm^{-1} for goethite; 224, 293, 412, 610 and $1,330\text{ cm}^{-1}$ for hematite). All three zones for each sample were analysed by X-ray powder diffraction (XRD) using the $<2\text{-}\mu\text{m}$ oriented phases to determine the composition of the finest clay assemblage and its variability towards the redox front. The XRD patterns of disoriented powders were also carried out to identify non-clays minerals. The XRD data were collected with a D8 Bruker diffractometer with $\text{Co-K}\alpha 1$ radiation ($\lambda = 1.7902\text{ \AA}$). Operating conditions were 35-kV accelerating voltage, 45-mA intensity, step scanning at $0.035^\circ(2\theta)$ intervals, 3-s counting time, $3\text{--}75^\circ(2\theta)$ for disoriented powders and $3\text{--}40^\circ(2\theta)$ for oriented slides. X-ray diffraction patterns were also recorded on air-dried oriented samples on ethylene glycol vapour (12 h at room temperature) saturated samples and after heating at 550°C for 4 h (550°C) to identify the clay minerals.

Results

Petrography and mineralogy

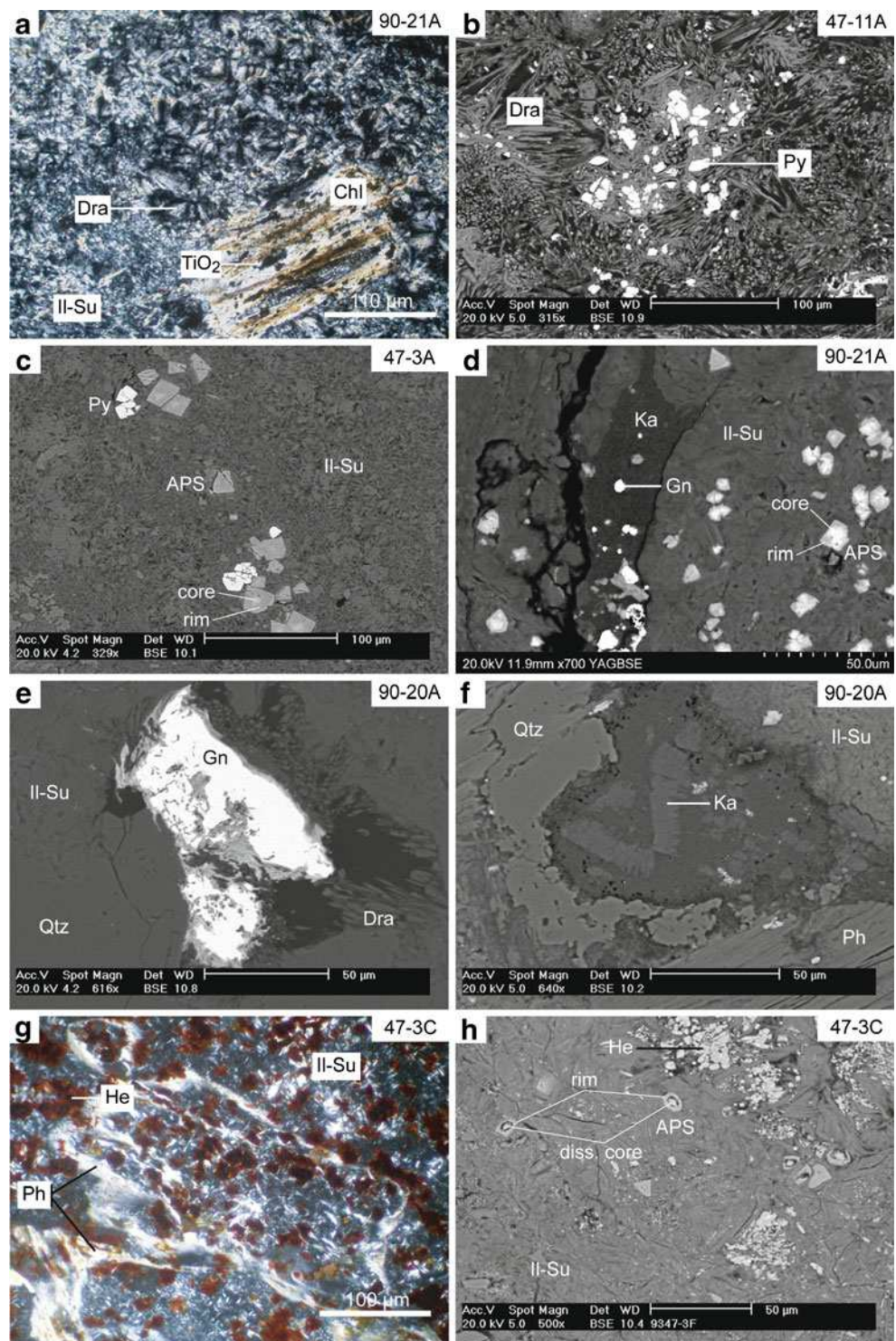
White-green zone

The WGZ mainly consists of a microcrystalline matrix composed of illite and sudoite. The different phases are hardly identifiable by optical or electron microscopy (Fig. 4a). Dravite is also observed in variable amounts as spherules, more or less well crystallised, within the illite–sudoite matrix (Fig. 4b). Primary rock-forming minerals such as feldspars, biotite, phengite or retrograde chlorite are locally preserved. Quartz crystals are generally preserved but may be locally dissolved, and the cavities may be filled with euhedral hydrothermal quartz crystals. APS minerals, such as were previously described mainly from the Athabasca Basin sandstone (Quirt et al. 1991; Gaboreau et al. 2005, 2007; Mwenifumbo and Bernius 2007), are common in the altered basement. However, close to the U redox front, most APS minerals have remarkable elemental zoning clearly seen in BSE images, with a core richer in high Z elements and with several overgrowths (Fig. 4c, d). Two types of sulphides are commonly visible in the WGZ, namely weakly altered, locally abundant cubic pyrite crystals and galena crystals finely disseminated in the altered matrix (Fig. 4c, e). The two sulphides are rarely spatially associated. Zircon, apatite and monazite crystals occur locally in this zone, but monazite crystals are moderately to strongly altered. Three WGZ samples contain kaolinite crystals (samples 47-3, 90-20 and 90-21). Kaolinite occurs as finely crystallised masses in vugs or fractures, locally associated with galena (Fig. 4d), and as characteristic booklets infilling quartz dissolution cavities (Fig. 4f). However, the amount of kaolinite relative to illite and sudoite is small, as confirmed by XRD.

Uranium front

The U front is developed within the illite–sudoite matrix, which is not altered. U-bearing minerals are mainly finely disseminated, microcrystalline ($<500\text{ }\mu\text{m}$) pitchblende (UO_2) and coffinite (USiO_4). They occur in voids, along cleavage planes of preserved minerals, as cavity infillings and as coatings around previous minerals (Fig. 5). Pitchblende coatings are the most commonly developed habit and are visible around pyrite, galena, anatase and zircon crystals. In most samples, pitchblende rim galena (Fig. 5d), but the pyrite–pitchblende association is also observed (sample 47-11, Fig. 5a). Sulphides are moderately to strongly corroded where they display such coasts. Pitchblende–zircon and pitchblende–anatase associations (samples 47-11 and 47-3, Fig. 5h) are rare. Uranium oxides

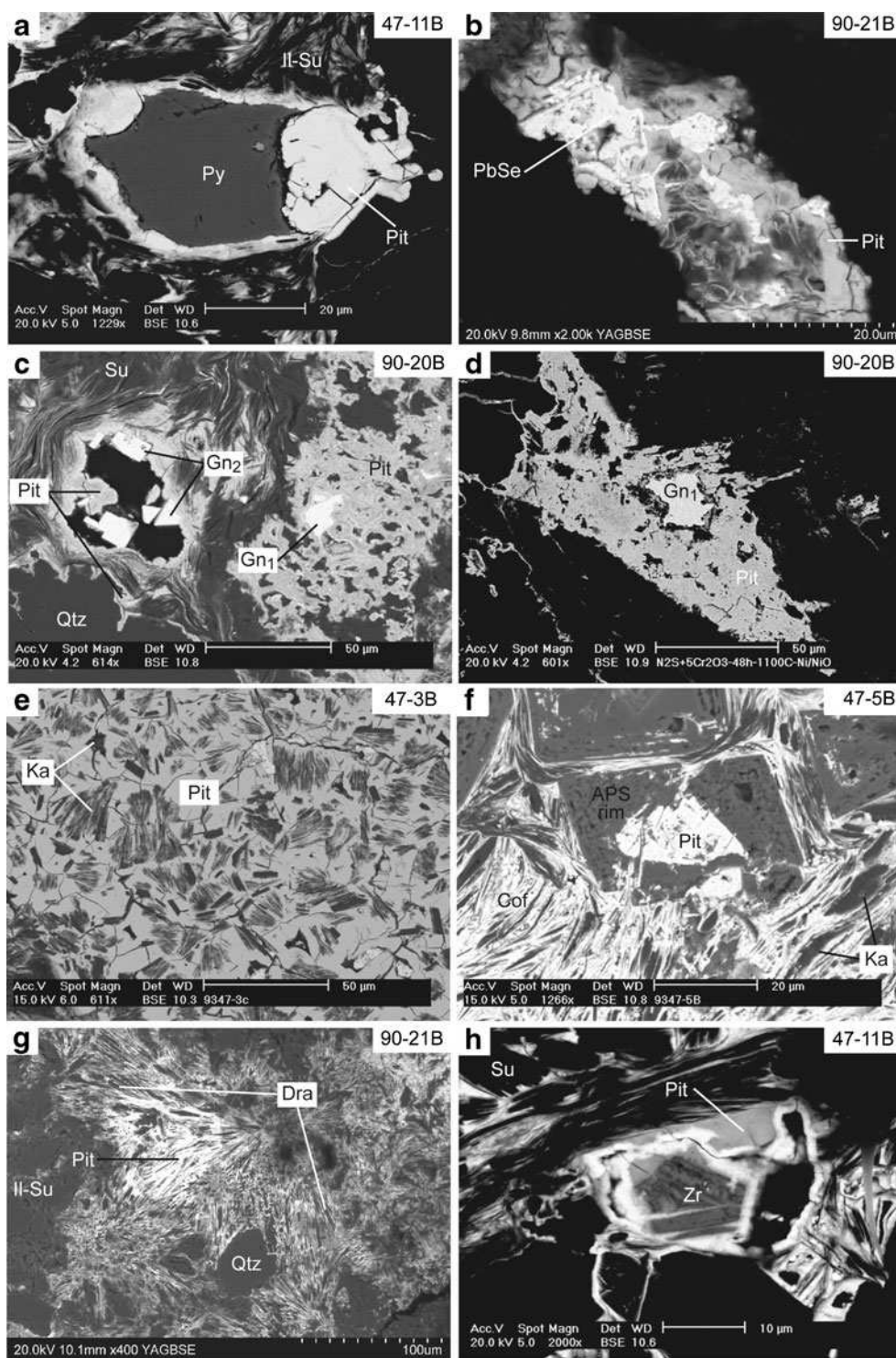
Fig. 4 Backscatter electron (BSE) images of typical mineral assemblages observed in the WGZ and RZ of the studied uranium redox fronts. **a** Illite- and sudoite-rich alteration matrix (*Il-Su*) in the WGZ of sample 90-21. Dravite (*Dra*, Mg-tourmaline) is often associated to illite and sudoite. Residual retrograde chlorite (*Chl*) is visible with new formation of titanium oxides (*TiO₂*) derived from biotite alteration. **b** Dravite-rich zone with euhedral pyrite (*Py*) clusters in the WGZ of sample 47-11. **c** Illite- and sudoite-rich alteration matrix with pyrite and aluminophosphate-sulphate minerals (*APS*) in the WGZ of sample 47-3. The majority of APS are euhedral and zoned with a chemically distinct core and rim. **d** Illite and sudoite-rich alteration matrix with APS and pyrite minerals. The matrix is crosscut by a kaolinite (*Ka*) and galena (*Gn*) vein. **e** Partly dissolved and altered galena crystal (*Gn*) in the WGZ of sample 90-20. Quartz (*Qtz*) is preserved. **f** Euhedral kaolinite crystal in quartz (*Qtz*) dissolution cavity in the WGZ of sample 90-20. Phengite (*Ph*) has no visible alteration features. **g** Illite and sudoite-rich alteration matrix with residual phengite superimposed by hematite (*He*) crystals in the RZ of sample 47-3. **h** Illite and sudoite-rich alteration matrix with disseminated APS minerals and clusters of hematite in RZ of sample 47-3. The core of euhedral APS mineral is partially to totally dissolved (*diss. core*), whereas rim is unaltered



partially fill the porosity in the illite–sudoite matrix, in retrograde chlorite, and in phengite- and dravite-rich zones (Fig. 5g). The zoned APS (core and overgrowth) observed in the WGZ near the UF are partly preserved with corroded cores which commonly replaced by pitchblende (Fig. 5f). Fractures with pitchblende infilling crosscut some pegmatite samples. The sulphides are more abundant within the U

front or in the vicinity of the front (up to several tens of centimetres away) than in the WGZ. A late galena generation (*Gn₂*, Fig. 5c) occurs close to and postdates the mineralisation. Clausthalite (*PbSe*) is locally associated with pitchblende (sample 90-21, Fig. 5b). Hematite and goethite are well developed in UF samples and impregnate the preexisting texture. Pitchblende is systematically

Fig. 5 BSE images of the various uranium minerals in the UF zone of the uranium redox fronts. **a** Zoned pitchblende (*Pit*) developed around partially dissolved pyrite (*Py*) in the illite and sudoite-rich (*Il-Su*) alteration matrix of sample 47-11. **b** Pitchblende associated with clausthalite (*PbSe*) in sample 90-21. **c** Pitchblende overgrowths around partially dissolved galena (*Gn*) associated with pitchblende crystallisation in a cavity and quartz (*Qtz*) dissolution zone. A second generation of euhedral galena (*Gn*₂) covers pitchblende minerals. Sample 90-20. **d** Pitchblende developed around partially dissolved galena of first generation in sample 90-20. **e** Cavity filled by sooty pitchblende cementing kaolinite (*Ka*) in sample 47-3. **f** Alumino-phosphate-sulphate (*APS*) mineral in kaolinite and coffinite-filled (*Cof*) cavity where the former APS core is totally dissolved and replaced by pitchblende. The APS rim (*APS rim*) is only slightly altered. Sample 47-5. **g** Dravite (*Dra*) and quartz-rich (*Qtz*) zone in illite and sudoite-rich alteration matrix in sample 90-21. The porosity between dravite grains is filled by pitchblende. **h** Pitchblende overgrowths around a corroded zircon (*Zr*) crystal in sample 47-11



encased by a goethite halo, giving to this zone its characteristic brownish colour (Fig. 1b).

Red zone

The red zone is characterised by a strong concentration of hematite and absence of goethite. Hematite is pervasively

disseminated within the preexisting altered zone, which consists of an illite–sudoite–dravite matrix, retrograde chlorites and phengites (Fig. 4g). The degree of alteration in the residual primary minerals is identical to that observed in the WGZ or UF. Zircon and apatite are well preserved. The illite–sudoite matrix, except the presence of hematite crystallisation, is texturally identical to that in the other

zones (WGZ and UF), but sulphides observed in the WGZ and UF are totally dissolved. The core of the APS crystals is partially to totally dissolved, whereas overgrowths are preserved (sample 47-3, Fig. 4h). None of the U-rich minerals from the UF are found in the red zone.

Kaolinite-rich zone

A kaolinite-rich assemblage can crosscut the three previously described zones of the redox front (Fig. 1c). The mineralogical association of each zone is strongly affected by this late event with the replacement of the majority of the minerals by kaolinite. This is particularly visible in the RZ where hematite is strongly leached, resulting in a colour change from red to white (Fig. 6a, b). The illite–sудоite crystals from the illite–sудоite microcrystalline matrix are mostly replaced by kaolinite, which is the major constituent (up to 80 modal per cent) of the zone (Fig. 6c). Other minerals observed in the three zones of the redox front, namely quartz or APS overgrowths, are preserved (Fig. 6d). Calcite is potentially associated with kaolinite (Fig. 6b). Sooty pitchblende associated with kaolinite and APS phases occurs in dissolution cavities in primary quartz (Fig. 5e).

Crystal chemistry of the uranium oxides and APS minerals

The composition of the U-rich minerals from the UF of all samples varies from U oxide to coffinite (Table 2). The less

altered pitchblendes define a well-characterised cluster with rather low Pb and Si contents (0.32–2.43 wt.% PbO, 0.9–1.6 wt.% SiO₂, Fig. 7), but high Ca contents (3.6–4.7 wt.% CaO). Si, Ca and Pb contents are quite constant within one sample, but can greatly differ between samples (e.g. samples 90-7, 90-20 and 47-3). Samples 47-11 and 90-21 contain pitchblendes with higher Pb contents. The inverse correlation between Pb+Ca and Si (Fig. 7) shows that Pb and Ca losses are associated with silica enrichment. P contents slightly increase with increasing silica content. Sooty pitchblendes in kaolinite-rich zones have low Pb contents (0–0.32 wt.% PbO, samples 47-3 and 47-5).

Two types of REE patterns for pitchblende were obtained by ion microprobe analysis of Eagle Point and P-Patch U oxides. Samples 47-3 (P-Patch) and 90-20 (Eagle Point) exhibit similar bell-shaped patterns centred on Tb and Dy, a strong negative Eu anomaly and LREE abundances (except for La, Fig. 8). Their HREE/LREE ratios are higher than 1 (2.4–4.04, Table 3). The U oxides in sample 90-7 (Eagle Point) have the same strong negative Eu anomaly and bell-shaped curve centred on Tb and Dy, but with much lower HREE abundances and higher LREE content. Furthermore, the HREE/LREE ratio is lower than 1 (0.16). Notably, the REE patterns of the U oxides are independent of the host rock lithology (pelitic gneisses or pegmatoids) and location (deposit).

The chemical composition of APS represents a solid solution between the svanbergite (Sr-rich), woodhouseite (Ca-rich), goyazite (Sr-rich) and florencite (LREE-rich)

Fig. 6 Photomicrograph and BSE images of typical mineral assemblages observed in the kaolinite-rich zones crosscutting the uranium redox fronts.

a, b Red zone (RZ) mineralogy replaced by a kaolinite-rich assemblage. The hematite (*He*) impregnation is leached and the illite–sудоite (*Il-Su*) matrix is replaced by kaolinite (*Ka*) crystals. Calcite (*Cal*) is associated with kaolinite. Quartz (*Qtz*) are preserved. **c** Detail of **b** showing the replacement of the illite–sудоite matrix and the hematite impregnation of the RZ by kaolinite crystals. Kaolinite can represent up to 80% of the new mineralogy. **d** Kaolinite-rich zone where the illite–sудоite matrix is almost totally replaced by kaolinite. APS crystals (*APS*), only composed of LREE-depleted overgrowth (*rim*), are preserved

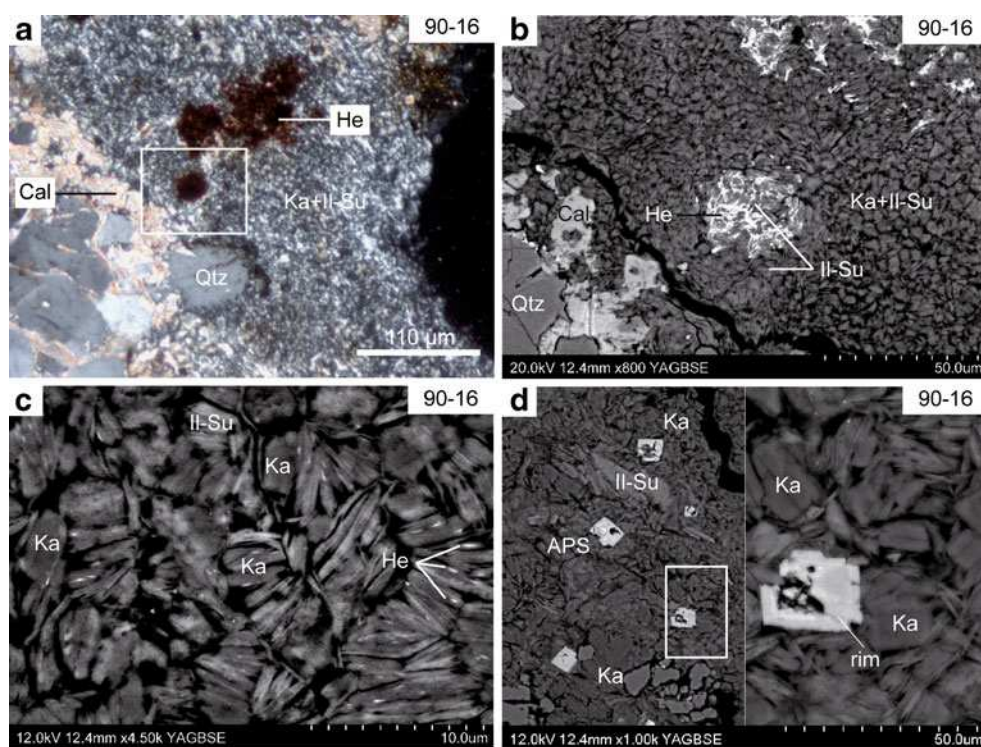


Table 2 Chemical composition of pitchblende and coffinite in the uranium redox front samples

Deposit sample analyses mineral	P-Patch												Eagle Point							
	47-11		47-11		47-11		47-5		47-3		47-4		90-7		90-20		90-20		90-21	
	18 Pit	σ	13 Pit	σ	7 Cof	σ	21 Pit	σ	19 Pit	σ	2 Cof	σ	38 Pit	σ	17 Pit	σ	3 Cof	σ	3 Pit	σ
Al ₂ O ₃	1.02	0.56	0.64	0.49	1.20	0.09	2.75	1.64	0.18	0.06	0.86	0.01	0.17	0.07	0.19	0.11	3.21	4.20	0.99	1.11
SiO ₂	5.73	1.81	4.02	0.68	13.06	1.96	7.67	2.04	1.23	0.25	12.92	0.68	0.86	0.24	1.62	0.30	11.68	4.35	3.75	0.72
P ₂ O ₅	0.46	0.31	0.53	0.08	0.50	0.29	0.69	0.25	0.54	0.05	1.51	0.21	0.53	0.09	1.00	0.19	1.10	0.44	1.50	0.03
SO ₂	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–	0.25	–	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–
CaO	2.72	0.35	3.19	0.18	2.48	0.47	2.45	0.29	3.62	0.44	1.64	0.34	4.67	0.35	4.74	0.64	4.18	1.11	2.06	0.19
V ₂ O ₃	<D.L.	–	0.35	0.07	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–	0.51	0.07	0.62	0.09	0.44	0.04	0.38	0.05
FeO	0.61	0.47	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–
MgO	0.18	0.02	n.a	–	n.a	–	0.36	0.26	0.10	0.02	0.11	0.07	0.08	0.02	0.12	0.04	0.41	0.38	0.19	0.21
MoO ₃	<D.L.	–	n.a	–	n.a	–	0.27	0.07	0.19	0.12	1.28	1.21	0.20	0.06	0.24	0.10	0.40	0.06	0.17	0.09
ZrO ₂	3.00	0.98	<D.L.	–	2.20	1.17	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–	1.21	0.26
K ₂ O	n.a	–	n.a	–	n.a	–	0.64	0.23	0.41	0.05	n.a	–	0.42	0.09	n.a	–	n.a	–	n.a	–
Na ₂ O	n.a	–	n.a	–	n.a	–	0.47	0.11	0.45	0.11	n.a	–	0.41	0.05	n.a	–	n.a	–	n.a	–
TiO ₂	<D.L.	–	n.a	–	n.a	–	<D.L.	–	n.a	–	<D.L.	–	0.11	0.04	<D.L.	–	<D.L.	–	1.82	0.11
Nd ₂ O ₃	–	–	0.18	0.01	0.36	0.11	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–	<D.L.	–
PbO	1.34	0.24	0.60	0.11	<D.L.	–	<D.L.	–	0.32	0.09	0.09	0.13	1.00	0.11	0.90	0.16	0.51	0.22	2.43	0.94
UO ₂	76.40	2.79	78.35	1.71	66.69	1.23	78.03	5.40	85.05	2.64	73.20	1.58	85.96	3.10	83.73	1.78	67.64	9.17	77.57	0.93
Total	91.46		87.86		86.50		93.32		92.09		91.86		94.92		93.15		89.57		92.08	

Detection limits (in wt.%): Al=0.08, Si=0.08, P=0.04, S=0.07%, Ca=0.11%, V=0.14%, Fe=0.2%, Mg=0.04%, Mo=0.12%, Zr=0.26%, K=0.1%, Na=0.11%, Ti=0.05%, Nd=0.51%, Pb=0.25%, U=0.55%

Pit pitchblende Cof coffinite, σ standard deviation, <D.L. below detection limit, n.a not analysed

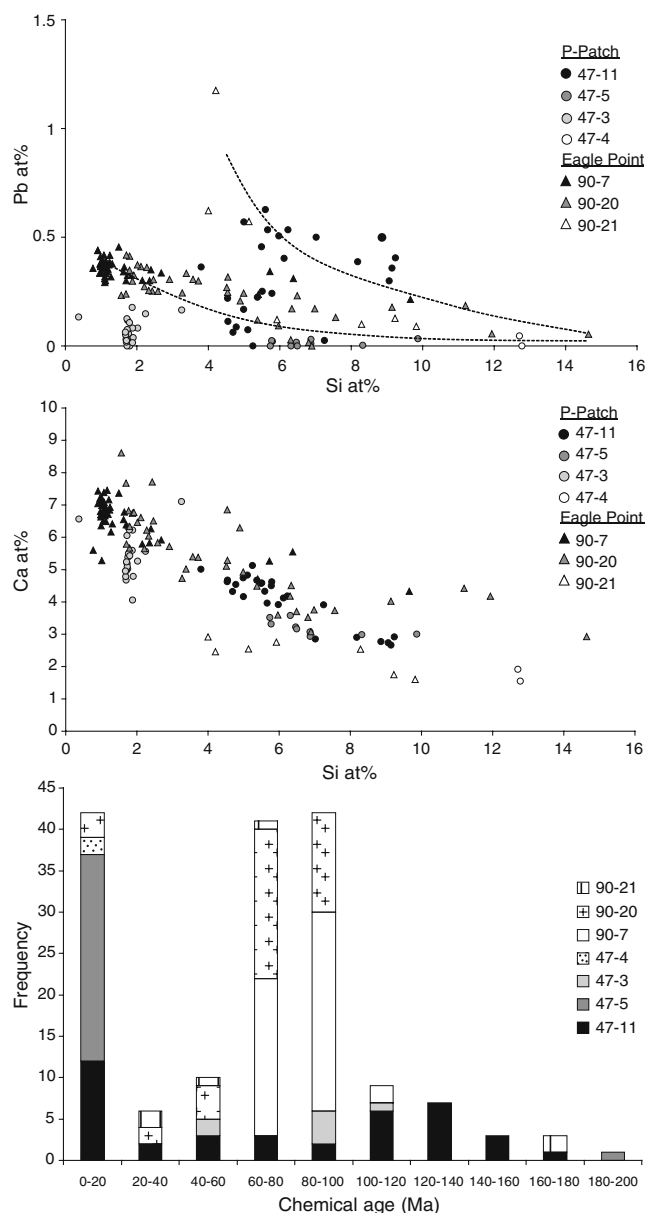


Fig. 7 Chemical compositions and associated chemical ages for pitchblende and coffinite in the uranium redox fronts samples (data from Table 2). Pb, Si and Ca contents (at.%, upper and middle) for pitchblende and coffinite analysed in samples 47-11, 47-5, 47-3, 47-4 (P-Patch deposit), 90-7, 90-20 and 90-21 (Eagle Point deposit). Two Si enrichment trends are visible in pitchblende in relation with the initial Pb content (*upper part*). Histogram of the chemical age calculated from pitchblende and coffinite analysis using Bowles (1990) formula modified by Kister (2003) (*lower part*)

end-members (Table 4; Gaboreau et al. 2005, 2007). The cores are characterised by high LREE and P contents and low S and Sr contents compared to the zoned overgrowths. Florencite end-member compositions dominate in the core, with high LREE (4.09–10.43 wt.% Ce_2O_3), P (19.45–23.10 wt.% P_2O_5) and Th (0.38–0.98 wt.% ThO_2) contents, whereas in the overgrowths, svanbergite dominates with

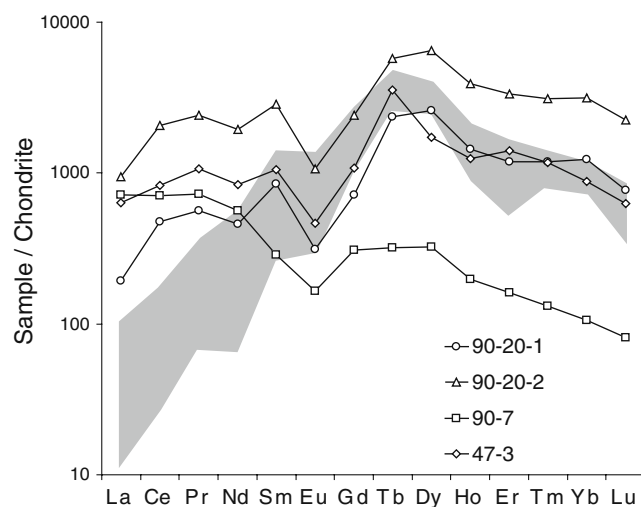


Fig. 8 Chondrite-normalised REE patterns of pitchblende in the uranium redox front samples of Eagle Point (90-20 and 90-7) and P-Patch (47-3) deposits, obtained by SIMS (see “Methodology” for details). Two analysis were completed on sample 90-20 (90-20_1 and 90-20_2). The grey zone corresponds to the unconformity-related uranium oxide reference chondrite-normalised REE patterns from the Eagle Point deposit (Mercadier 2008; Mercadier et al. 2009). Analytical data are presented in Table 3

Table 3 REE contents for pitchblende in redox front 47-3, 90-20 and 90-7 samples analysed by ion microprobe (in ppm)

Sample analyses	47-3	90-20		90-7
		90-20_1	90-20_2	
La	634	194	947	117
Ce	824	474	2,070	363
Pr	1,066	566	2,410	58
Nd	838	461	1,958	229
Sm	1,052	844	2,871	39
Eu	462	311	1,062	9
Gd	1,079	713	2,431	20
Tb	3,563	2,351	5,721	10
Dy	1,729	2,600	6,450	67
Ho	1,241	1,448	3,931	9
Er	1,407	1,191	3,332	19
Tm	1,168	1,188	3,110	2
Yb	884	1,235	3,165	2
Lu	627	775	2,238	2
Total REE	16,575	14,350	41,696	945
LREE	4,876	2,849	11,318	815
HREE	7,056	8,437	22,226	101
HREE/LREE	1.45	2.96	1.96	0.12

LREE = La+Ce+Pr+Nd+Sm+Eu, HREE = Dy+Ho+Er+Tm+Yb+Lu

Table 4 Chemical composition of zoned APS minerals in redox front 47-3 and 47-5 samples

Sample analyses zone	47-5C		47-5C		47-3A		47-5B		47-3D		47-5C		47-5C		47-3A		47-5B		47-3D	
	4	σ	5	σ	2	σ	13	σ	3	σ	8	σ	10	σ	6	σ	34	σ	3	σ
	WGZ_core		WGZ_core		WGZ_core		UF_core		RZ_core		WGZ_rim		WGZ_rim		WGZ_rim		UF_rim		RZ_rim	
SrO (wt.%)	2.36	1.64	8.54	2.33	8.58	0.42	7.11	2.86	9.08	2.65	14.21	5.26	12.09	7.47	15.24	5.41	15.65	2.05	14.57	1.30
CaO	2.53	0.36	2.70	0.55	2.35	0.26	2.72	0.41	2.03	0.34	2.46	0.78	2.30	0.64	1.93	0.37	2.37	0.46	2.29	0.64
La ₂ O ₃	5.52	0.74	4.00	0.59	1.92	0.20	5.02	1.06	3.77	1.93	0.37	0.23	0.34	0.21	0.29	0.15	0.59	0.70	0.67	0.50
Ce ₂ O ₃	10.43	1.22	6.51	1.09	4.09	0.74	7.69	2.39	6.92	3.30	1.05	0.73	0.84	0.39	1.67	2.32	1.12	1.25	1.05	0.58
Pr ₂ O ₃	0.27	0.24	0.17	0.18	0.11	0.08	0.13	0.14	0.03	0.05	0.13	0.16	0.07	0.09	0.17	0.27	0.12	0.12	0.17	0.13
Nd ₂ O ₃	3.14	0.27	1.29	0.78	2.49	1.25	1.74	0.85	1.79	0.54	0.74	0.56	0.87	0.66	0.66	0.33	0.76	0.31	1.50	0.18
SmO	0.31	0.07	0.15	0.08	0.15	0.04	0.17	0.10	0.18	0.11	0.14	0.15	0.21	0.18	0.30	0.18	0.07	0.10	0.34	0.21
ThO ₂	0.85	0.28	0.98	0.78	0.80	0.27	0.86	0.47	0.38	0.25	0.07	0.11	0.09	0.15	0.18	0.11	0.20	0.20	0.17	0.09
UO ₂	<D.L.		<D.L.		<D.L.		1.26	2.51	<D.L.		<D.L.		<D.L.		<D.L.		0.63	0.87	<D.L.	
Al ₂ O ₃	29.07	0.62	27.64	1.72	27.76	0.31	29.03	1.53	28.64	2.36	31.04	1.12	31.07	1.18	31.26	1.35	29.93	2.02	31.17	0.56
P ₂ O ₅	23.10	1.29	20.41	0.77	19.45	1.45	20.91	1.26	21.78	1.24	21.05	1.24	20.62	0.85	21.24	1.12	18.95	1.94	20.90	0.59
SO ₃	0.93	0.32	3.04	0.64	3.79	0.11	1.67	1.47	4.79	0.42	8.83	1.51	9.21	1.43	8.48	1.09	9.39	1.50	8.02	0.70
SiO ₂	0.59	0.16	0.78	0.12	0.55	0.17	0.84	0.19	1.20	0.35	0.68	0.40	0.67	0.31	0.72	0.16	0.37	0.23	1.06	0.22
F	0.42	0.05	0.43	0.07	0.27	0.17	0.48	0.14	0.22	0.09	<D.L.		<D.L.		<D.L.		<D.L.		<D.L.	

The analysis is classified relatively to the zone where the APS were analysed (*WGZ* white-green zone, *UF* uranium front, *RZ* red zone) and the zonation between core and rim in the APS mineral. Detection limit (in wt.%): Sr=0.11, Ca=0.07, La=0.05, Ce=0.05, Pr=0.1, Nd=0.37, Sm=0.16, Th=0.11, U=0.1, Al=0.03, P=0.05, S=0.11, Si=0.04, F=0.08

σ standard deviation, <D.L. below detection limit

high S (8.02–9.39 wt.% SO_3) and Sr (12.09–15.65 wt.% SrO) contents (Fig. 9). The APS minerals also contain significant Si (0.37–1.20 wt.% SiO_2) and Ca (1.93–2.72 wt.% CaO) contents with little variation between core and overgrowth.

Whole rock geochemistry

The geochemical data are in Table 5 and illustrated in Figs. 10, 11 and 12. No significant variations of rock density or volume exist between the three zones of the redox front; therefore, no density correction is applied to the whole rock compositions. This result is confirmed by the invariability of the contents of the less mobile elements, such as Al, Ti, Zr, Th or Ta, in the three zones (Fig. 10). The compositions of the red zone and U front of sample

90-20 are normalised to that of the white-green zone to illustrate the element mobility associated with the formation of the redox front (Fig. 10). The evolution of the concentrations of six redox-sensitive elements (U, W, S, Mo, Se, Fe^{2+} and Fe_{total}) along the three zones of the redox fronts is represented in Fig. 11.

Major elements, Fe and Ca excepted, do not show any significant variations between the three zones for all the samples. The stable contents of K, Mg and Si reflect the preservation of the major silicate phases (mainly illite, sudoite, dravite and quartz) and of their relative proportions between the zones of the redox fronts. Total Fe ($\text{Fe}_2\text{O}_{3\text{T}}$) contents may reach one order of magnitude higher in the RZ and UF than in the WGZ, with a maximum content in the RZ (Fig. 10). Divalent Fe (FeO), principally reflecting the abundance of pyrite, is up to ten times more abundant in

Fig. 9 Chemical compositions of aluminophosphate-sulphate (APS) cores and overgrowth (rim) in the uranium redox front of 47-3 and 47-5 samples. LREE+P vs. Sr+S+Ca contents (upper part) and LREE vs. P/S ratio (lower part) diagram. LREE=La–Sm. Analytical data are presented in Table 4. $f\text{O}_2$ curve refers to Gaboreau et al. (2007)

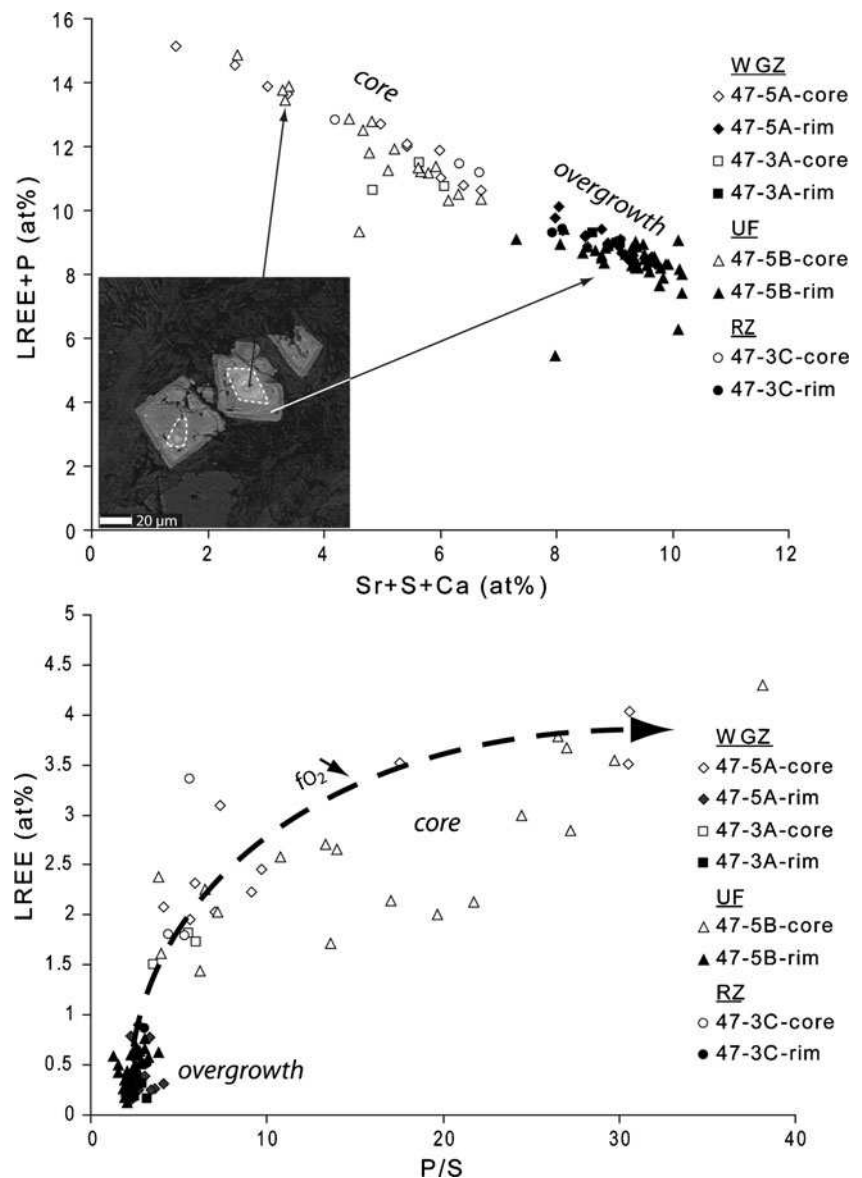


Table 5 Whole rock chemical composition of uranium redox front samples

Deposit sample description	Eagle Point						P-Patch										
	90-20C	90-20B	90-20A	90-21C	90-21 B	90-21A	47-3C	47-3B	47-3A	47-11C	47-11B	47-11A	47-4C	47-4B	47-4A	47-5B	47-5A
	Red zone	U front	w-g zone	Red zone	U front	w-g zone	Red zone	U front	w-g zone	Red zone	U front	w-g zone	Red zone	U front	w-g zone	U front	w-g zone
SiO ₂ (wt.%)	63.31		68.33	60.71		65.39	63.02		66.10	66.37		67.63	70.51		76.03		70.50
Al ₂ O ₃	16.18	14.92	18.26	16.75	18.42	20.54	16.12	15.34	18.90	14.88	15.17	15.36	16.07	15.16	15.22	12.63	16.37
Fe ₂ O ₃ T	4.16	3.98	0.47	8.70	4.08	0.35	6.79	5.15	0.32	2.58	1.83	1.22	5.29	1.22	0.15	1.12	0.72
FeO	<0.05	0.60	<0.05	<0.05	0.24	<0.05	0.09	0.45	<0.05	0.11	0.21	0.20	0.07	0.01	<0.05	0.24	0.06
MnO	0.06	0.01	0.01	0.01	0.01	0.01	0.03	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.02	0.01
MgO	2.49	1.46	1.63	1.74	1.34	1.71	2.41	2.10	4.02	4.32	4.31	4.88	1.19	1.04	1.42	1.46	2.21
CaO	0.67	0.42	0.18	0.22	0.28	0.13	0.20	0.32	0.09	0.42	0.54	0.41	0.07	0.21	0.07	0.20	0.24
Na ₂ O	0.09	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	0.24	0.25	0.13	0.20	<D.L.	0.11	0.12	<D.L.	0.08	<D.L.	0.13
K ₂ O	3.81	3.04	3.49	3.26	2.73	3.10	2.58	2.40	2.42	1.48	1.13	1.20	3.70	3.66	3.62	2.62	3.00
TiO ₂	0.59	0.52	0.57	0.47	0.48	0.47	0.44	0.75	0.58	0.68	0.64	0.66	0.01	<D.L.	0.01	0.54	0.72
P ₂ O ₅	0.08	0.13	0.06	0.16	0.15	0.07	0.06	0.08	0.06	0.18	0.21	0.22	0.03	<D.L.	<D.L.	<D.L.	0.17
L.O.I	7.19	7.16	6.68	7.13	8.25	7.13	7.94	7.76	7.03	9.20	8.44	7.34	3.63	4.64	3.59	5.08	5.60
Total	98.62		99.66	99.14		98.88	99.83		99.66	100.32		99.02	100.62		100.20		99.66
Fe ₂ ⁺ /Fe ₃ ⁺	0.00	0.20	0.00	0.00	0.07	0.00	0.01	0.11	0.00	0.05	0.15	0.22	0.01	0.01	0.00	0.31	0.10
As (ppm)	<D.L.	42.0	45.5	2.8	16.0	36.3	3.0	<D.L.	2.3	2.2	28.8	20.0	<D.L.	6.1	<D.L.	<D.L.	1.5
Ba	84.4	83.4	47.9	72.0	62.2	55.9	190	246	43.4	309	195	75.3	61.0	175	28.0	198	64.2
Be	5.7	14.6	6.5	10.6	8.3	6.1	4.1	<D.L.	3.9	5.3	<D.L.	3.5	1.9	<D.L.	1.6	<D.L.	3.4
Bi	3.5	2.9	2.4	4.5	8.5	3.2	7.5	8.0	0.3	82.5	12.4	13.3	0.8	<D.L.	<D.L.	2.5	0.5
Cd	0.1	<D.L.	2.5	0.5	1.5	1.2	0.5	0.5	0.6	0.3	0.7	1.1	<D.L.	0.9	2.0	<D.L.	0.5
Co	<D.L.	8.4	14.6	4.8	3.8	9.9	0.6	<D.L.	1.3	1.4	7.4	5.2	0.8	3.4	3.0	<D.L.	0.9
Cr	64.9	85.6	60.7	<D.L.	14.6	<D.L.	44.4	74.2	70.4	82.1	102	85.0	<D.L.	<D.L.	<D.L.	72.4	86.0
Cs	2.5	1.4	1.3	1.9	1.5	1.0	1.2	1.3	0.3	1.6	1.1	1.0	0.4	<D.L.	0.2	0.9	0.6
Cu	8.3	<D.L.	7.0	8.5	10.2	12.4	4.2	<D.L.	<D.L.	34.1	<D.L.	5.4	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.
Ga	41.7	37.5	37.6	45.9	38.2	42.4	23.0	22.8	26.7	25.9	25.1	25.9	15.3	13.5	16.0	17.3	23.3
Ge	3.4	8.6	2.2	3.7	3.7	2.6	2.9	5.8	1.6	3.0	4.6	2.1	2.0	5.1	1.2	5.9	1.5
Hf	4.4	3.7	3.9	14.2	13.3	13.5	8.6	9.4	5.9	8.0	10.0	9.2	0.1	0.1	0.1	7.9	12.0
Mo	6.7	567	908	40.6	245	497	17.1	21.8	367	5.1	324	273	3.2	354	744	77.6	31.2
Nb	12.3	10.4	11.0	19.6	19.7	20.8	9.3	16.8	12.0	15.1	13.4	14.6	0.7	0.3	0.3	13.3	21.9
Ni	40.8	71.9	67.1	17.9	26.8	57.8	22.4	26.6	42.8	23.9	50.9	40.4	10.7	24.4	17.7	18.9	18.5
Pb	284	1214	99.7	231	384	87.6	2006	1031	52.2	165	288	87.5	86.8	920	72.0	792	55.4
Rb	83.4	63.4	71.5	74.2	58.3	65.3	37.6	37.8	29.0	43.5	32.4	32.4	43.2	45.8	51.0	37.7	38.5
S (%)	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.5	<0.05	0.0	0.1	0.1	<0.01	0.0	0.0	0.0	0.2
Sb	0.9	4.0	1.6	0.6	1.1	1.8	2.6	3.5	0.3	<D.L.	8.1	4.9	0.4	3.9	0.7	4.4	0.4

Se	0.0	2.6	6.5	0.1	0.2	5.9	3.8	3.6	11.3	4.1	0.5	9.9	0.1	34.4	15.3	2.3	3.0
Sn	1.9	3.0	3.1	1.7	1.9	2.6	3.3	2.3	1.0	2.5	1.9	1.9	1.2	2.1	1.3	2.1	3.1
Sr	122	129	129	351	301	307	179	114	409	49.5	63.8	37.7	37.3	63.0	21.7	221	460
Ta	1.1	0.8	0.9	0.9	1.1	1.4	0.6	0.9	0.6	1.5	0.9	1.0	0.1	0.1	0.0	0.9	1.7
Th	7.2	8.2	9.7	55.3	72.2	51.6	6.0	10.8	3.2	6.5	14.7	17.1	0.8	0.3	0.5	12.7	19.8
U	673	25932	322	6344	12228	107	15760	30900	13.0	372	23913	2042	50.5	24940	191	25820	648
V	404	332	321	510	618	296	567	525	143	143	207	181	105	209	50.0	443	177
W	3.1	24.9	1.7	8.7	10.7	1.7	17.1	28.2	0.4	0.8	13.2	1.8	1.9	15.6	<D.L.	12.5	1.1
Y	25.9	130.2	7.4	36.2	27.3	11.0	78.6	201.9	3.4	26.1	71.2	19.1	3.5	50.1	0.6	56.7	6.1
Zn	<D.L.	<D.L.	10.6	14.7	<D.L.	13.0	12.2	<D.L.	<D.L.	10.4	<D.L.	9.8	<D.L.	<D.L.	<D.L.	<D.L.	11.2
Zr	160	137	148	595	485	574	330	366	200	274	470	350	3.9	<D.L.	2.1	373	411
La	15.5	29.0	17.1	97.8	75.4	69.0	25.1	36.6	17.0	3.7	31.0	8.0	1.1	2.9	1.1	35.2	36.6
Ce	32.9	89.2	36.1	197	141	132	79.0	88.6	33.9	33.2	110	21.2	3.0	5.8	2.7	57.4	72.2
Pr	2.6	13.3	3.7	21.2	13.7	13.0	17.6	14.6	4.7	2.7	15.1	3.0	0.4	1.3	0.3	10.8	8.3
Nd	9.5	54.4	12.1	67.5	43.0	39.1	82.2	69.5	20.3	12.5	59.0	13.1	1.8	8.6	1.0	44.3	30.3
Sm	1.6	19.5	2.0	12.5	7.7	5.0	50.0	31.4	5.9	5.2	13.2	3.3	0.9	5.3	0.1	14.3	5.2
Eu	0.3	2.5	0.6	1.6	1.2	1.1	7.3	4.5	1.0	1.4	3.8	0.7	0.3	1.7	0.2	3.2	0.6
Gd	2.3	20.7	1.5	8.3	5.7	2.7	48.0	51.6	4.3	6.6	17.8	4.1	1.2	11.9	0.1	16.3	2.9
Tb	0.5	7.8	0.4	2.5	1.7	0.5	21.8	18.2	0.4	2.5	4.0	0.8	0.3	2.4	0.0	5.5	0.3
Dy	3.3	58.0	2.6	17.9	12.2	2.9	118	102	1.0	15.5	19.9	4.2	1.7	11.7	0.1	30.6	1.4
Ho	0.6	8.7	0.4	2.6	1.7	0.5	13.0	14.0	0.1	2.1	2.9	0.7	0.2	1.6	0.0	4.0	0.2
Er	1.5	20.1	1.0	6.3	4.2	1.3	25.5	28.4	0.3	5.1	6.0	1.6	0.4	3.0	0.0	8.4	0.7
Tm	0.2	2.9	0.2	1.0	0.6	0.2	3.4	3.3	0.0	0.8	0.7	0.2	0.1	0.3	<D.L.	1.1	0.1
Yb	1.3	18.2	1.2	6.5	4.5	1.5	18.1	16.5	0.4	5.8	4.1	1.3	0.4	1.7	0.0	6.8	0.9
Lu	0.2	2.0	0.2	0.8	0.5	0.2	1.8	2.0	0.1	0.6	0.5	0.2	0.0	0.2	0.0	0.7	0.1

For each sample, the three analyses correspond to the three redox zones (red zone, uranium front and white-green zone)

<D.L. below detection limit

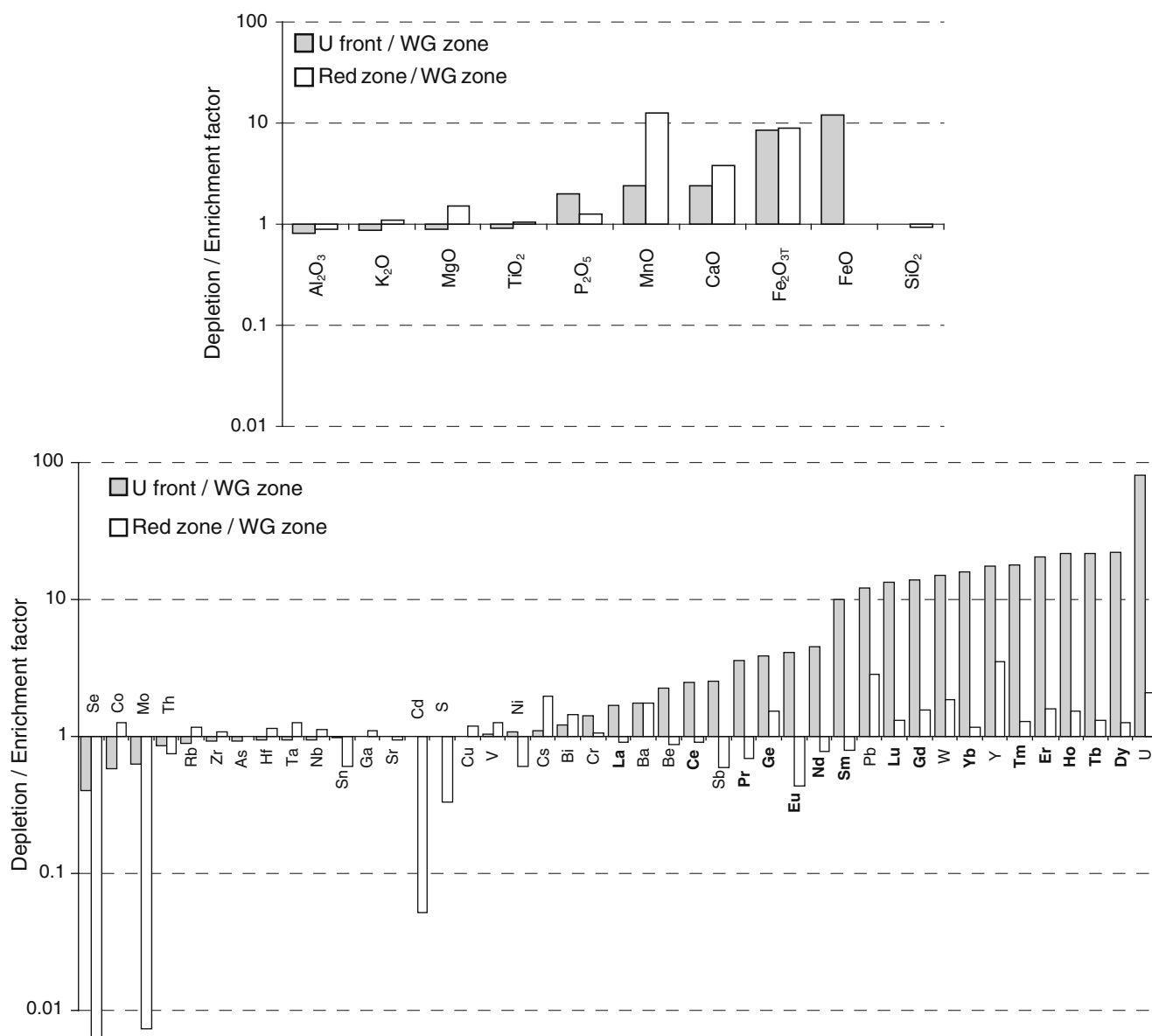


Fig. 10 Elemental depletion–enrichment factor for uranium front (U front, grey) and red zone (red zone, white) normalised to white-green zone (WG zone) for major elements (upper part) and trace elements

(lower part) of sample 90-20. Rare earth elements are symbolised with bold letters. Analytical data are given in Table 5

the UF than in WGZ or RZ (Fig. 11), whereas in the RZ, Fe^{3+} , expressed as hematite, is the dominant state for iron. Therefore, the higher $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of the UF reflects the abundance of pyrite and thus is an indirect measurement of the bulk oxidation state of the zone. Mn and P content variations cannot be considered as representative because of concentrations close to the detection limit in the three zones. The small gain in Ca in the RZ and UF (0.07–0.67 wt.% CaO) is explained by the Ca content of the U oxides, which are locally present in the RZ (due to U contamination from U oxides from the UF during zone separation), and by the crystallisation of late carbonates (especially sample 90-20).

Zr, Sr, Th, Ga, Nb, Sn, Ta and Th have homogeneous contents across the redox front profiles. U, REE, Pb, Y and W are systematically enriched in the RZ and/or UF compared to the WGZ, whereas Se, Mo and S are enriched in the WGZ and the UF zones in relation to the presence of clauthalite, sulphides, sulphates and possibly jordisite (amorphous MoS_2 , Fig. 11). Mo contents are ten times higher in the WGZ (up to 907.5 ppm) than in the two other zones and are still considerably higher than in WGZ away from the redox front (mainly <10 ppm).

U concentrations vary from 1.22 to 3.09 wt.% U in the UF, from 13 to 2,042 ppm in the WGZ and from 50 ppm to 1.6 wt.% U in the RZ. The high U contents for several

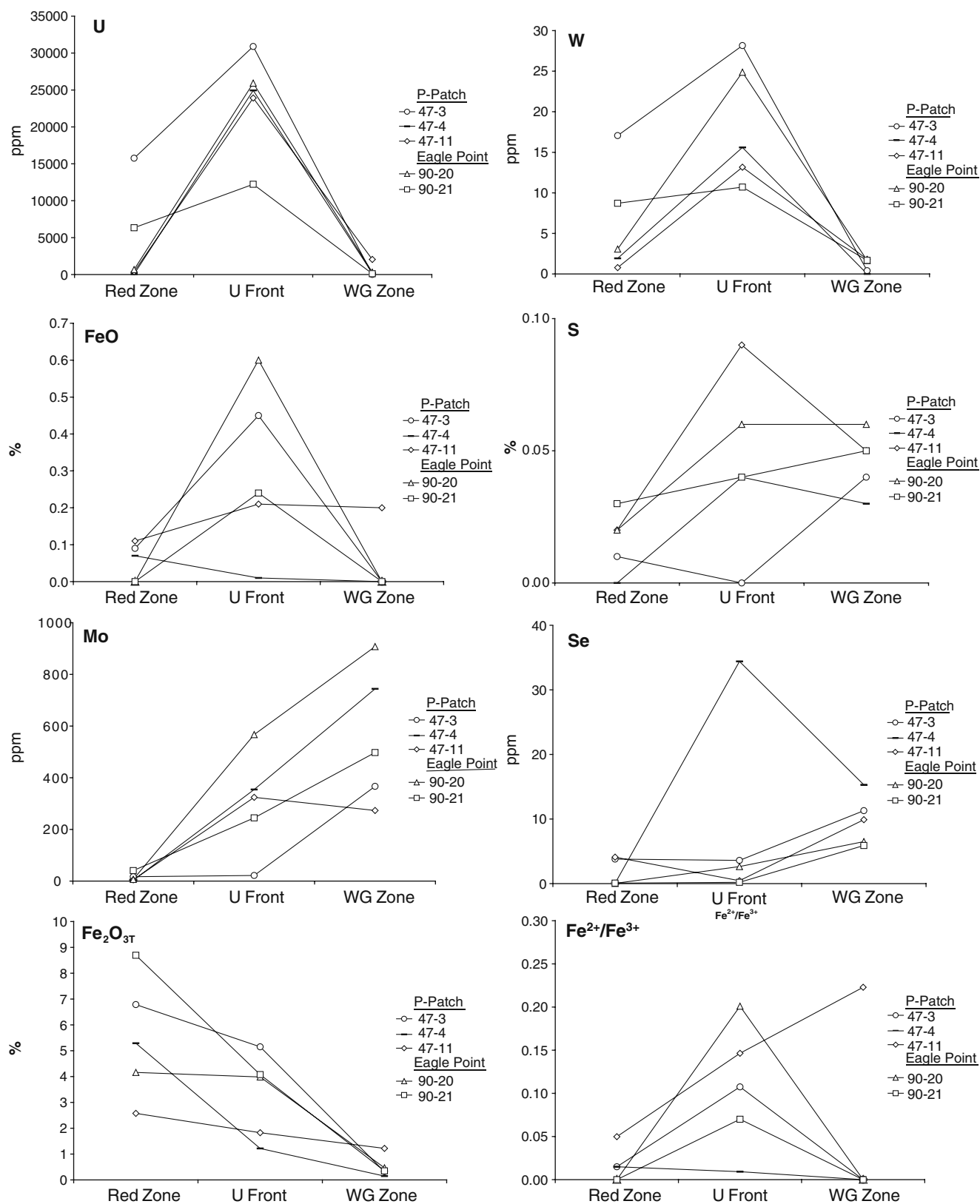


Fig. 11 U, W, Fe, S, Mo and Se content and distribution in the red zone (RZ), uranium front (U front) and white-green zone (WG zone) for the uranium redox fronts 47-3, 47-4, 47-11, 90-20 and 90-21.

Analytical data are given in Table 5. When FeO value was below the detection limit, the value 0 was used to repartition FeO and to calculate the Fe²⁺/Fe³⁺ ratio

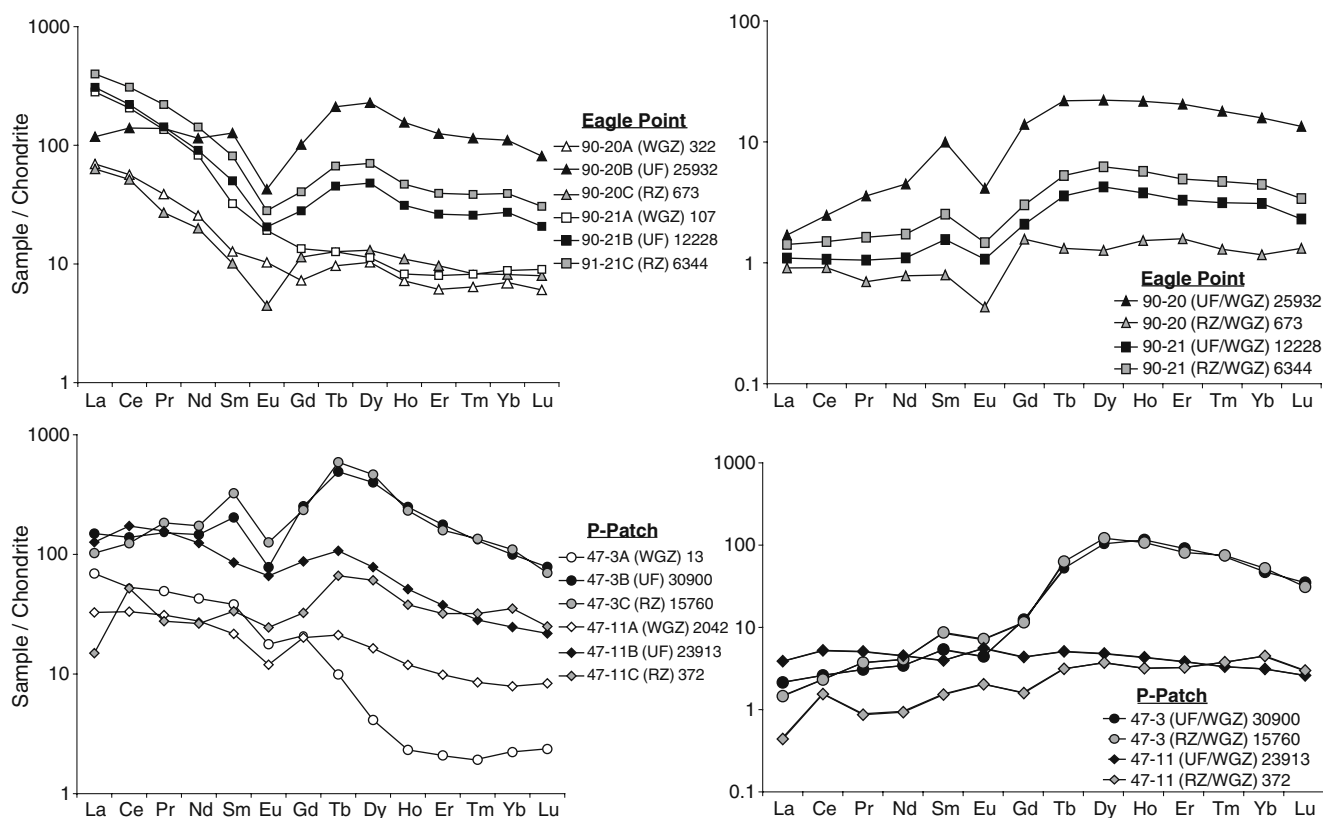


Fig. 12 Chondrite-normalised, whole-rock REE patterns for the three zones (WGZ, UF and RZ) of the uranium redox fronts for samples 90-20, 90-21 (Eagle Point deposit, *upper part*), 47-3 and 47-11 (P-Patch deposit, *lower part*). The value associated to each symbol corresponds

to uranium content (ppm) of each analysed zone. The two diagrams on the *right* show the REE enrichments of UF and RZ normalised to the WGZ content. WGZ white-green zone, UF uranium front, RZ red zone. Analytical data are given in Table 5

WGZ and RZ (samples 90-20, 47-11, 90-21, 47-3 and 47-5) are explained by a contamination from U oxides from the UF during sample preparation due to the small size of the samples and the complex shape of some of the redox fronts. Neither pitchblende nor coffinite crystals have been identified for the non-contaminated WGZ and RZ samples, but U is probably adsorbed on clay minerals or Fe–Ti oxides and Fe hydroxides.

The whole rock chondrite-normalised REE patterns of the WGZ display a negative Eu anomaly and LREE enrichment (Fig. 12) and are typical of the basement alteration halo associated with the unconformity-type mineralisation (Fayek and Kyser 1997). LREE abundance is controlled mainly by the APS phases, particularly their LREE-rich cores, and to a lesser extent by apatite and possible preserved monazite. A bulge at Tb and Dy exists in the REE patterns for samples 90-20 and 47-1 and is directly proportional to the inferred U mineral contamination during sample preparation in the WGZ. The REE patterns of the UF strongly differ from the WGZ with up to hundred times more total REEs and higher HREE (UF/WGZ ratios for HREE range from 2.61 to 107.4) than LREE (UF/WGZ ratio for LREE range from 1.05 to 9.95)

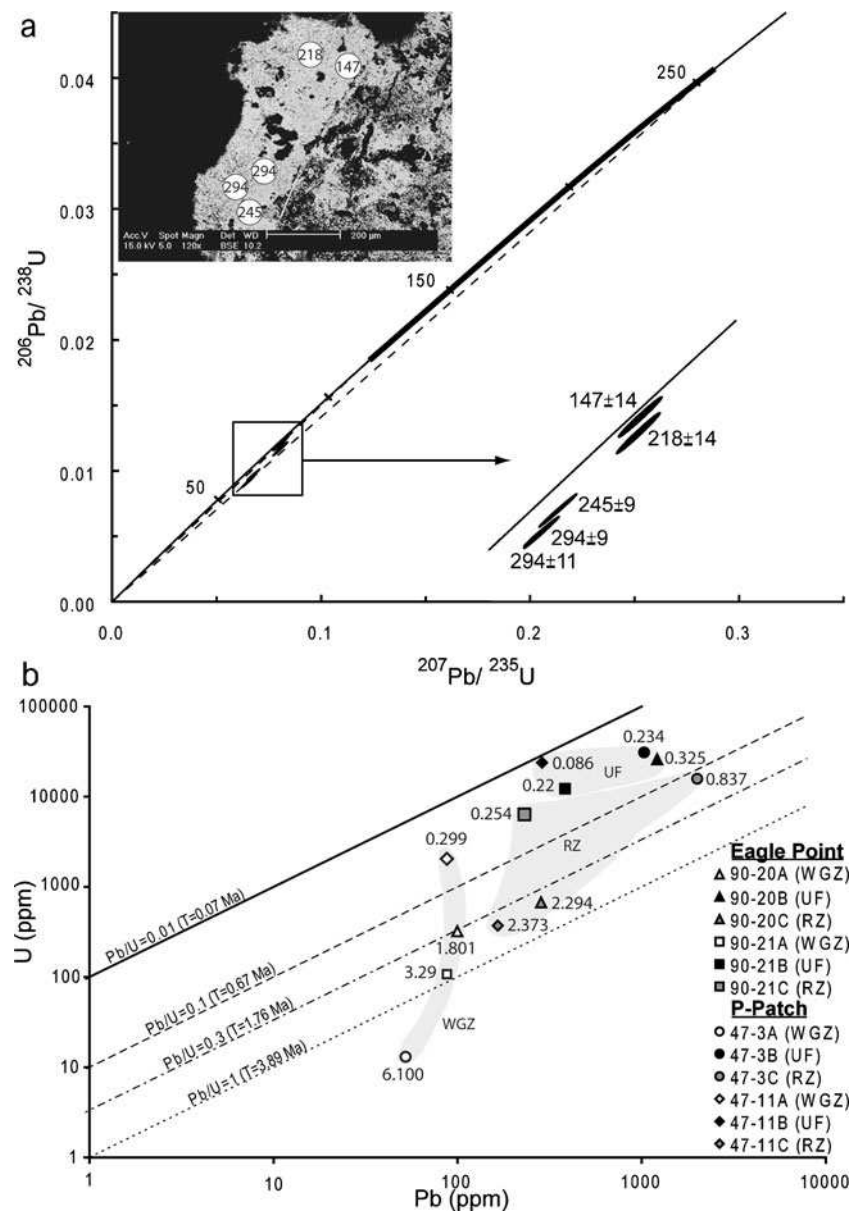
enrichment, the enrichments being centred on Tb and Dy (Fig. 12). Sample 90-21 contains anomalously high LREE contents relative to the other samples. Except this case, the REE patterns are mainly controlled by the presence of U oxides, as illustrated in Fig. 8. The REE patterns of the RZ are broadly parallel to those of the UF, but with up to ten times less REE (Fig. 12). As already described, the REE patterns of the RZ are directly dependent on its U mineral content, related to admixture of the UF during sample preparation (samples 47-3 and 90-21). In the contaminated RZ, REE contents are close to those in the UF, but for the U-poor samples, the contents are much lower and similar to WGZ REE contents.

U/Pb dating and U/Pb geochemistry

U/Pb dating of uranium oxides

Only one sample from the Eagle Point deposit has been dated (sample 90-7). In a Concordia diagram, the U–Pb isotopic compositions of the least altered pitchblende (Si-poor and Pb-rich) correspond to ages between 120 and

Fig. 13 **a** Concordia diagram showing the U/Pb isotopic analysis of pitchblende from sample 90-7. The *insert* is a BSE image of the pitchblende with the $^{207}\text{Pb}/^{206}\text{Pb}$ age at each analytical spot. The proposed upper intercept, using a lower intercept of zero, lies in a wide zone between 120 and 260 Ma. Analytical data are presented in Table 3. **b** Pb/U diagram for the three zones (WGZ, UF and RZ) of the uranium redox front for samples 90-20, 90-21 (Eagle Point deposit), 47-3 and 47-11 (P-Patch deposit). The value associated with each symbol corresponds to chemical age calculated from Bowles (1990) formula modified by Kister (2003) and expressed in Ga. Analytical data are given in Table 6



250 Ma. These ages are obtained if individual Discordia passing through zero is calculated for each analytical point (Fig. 13a). The $^{207}\text{Pb}/^{206}\text{Pb}$ ages yield nearly the same range of values (294 ± 11 Ma to 147 ± 14 Ma, Table 6). Considering the chemical homogeneity of sample 90-7 for the analysed zones (Table 2 and Fig. 7), all the analytical points can be considered as representative of the same crystallisation event. The oldest $^{207}\text{Pb}/^{206}\text{Pb}$ age could be interpreted as a minimum estimate of the age of pitchblende deposition in the Eagle Point redox front, ca. 300 Ma. All isotopic analyses are weakly to moderately discordant, indicating a small Pb loss after crystallisation. Other samples from the P-Patch and Eagle Point deposits do not match the requirements for analysis as homogeneous pitchblende was smaller than the analytical spot diameter.

Comparative whole rock and uranium oxides U–Pb geochemistry

In a Pb–U diagram (Fig. 13b), UF whole rock samples are characterised by low Pb/U values (0.01–0.1) corresponding to young chemical ages ranging from 86 to 325 Ma. This result is in good agreement with the isotopic ages and the chemical ages directly measured or calculated from the chemical composition of U oxides (Fig. 7) and thus indicates that U and Pb contents in the UF are nearly totally controlled by the uranium oxides. The majority of the calculated chemical ages for U oxides are <200 Ma (except for sample 90-21) and the distribution is bimodal (Fig. 7). The first group centred on 80–100 Ma corresponds to the less altered pitchblende crystals (samples 90-7, 90-20

Table 6 Analytical data for U–Pb analysis of pitchblende from sample 90-7

Sample analytical point	207Pb/206Pb	204Pb/206Pb	208Pb/206Pb	207Pb/235Pb	206Pb/238Pb	Correl.err	Age 207Pb/206Pb	Age 206Pb/238Pb	Age 207Pb/235Pb
3	0.0490 ± 0.0003	0.0000 ± 0.0000	0.0011 ± 0.0000	0.0812 ± 0.0029	0.0120 ± 0.0004	0.99	147 ± 14	77 ± 3	79 ± 3
4	0.0505 ± 0.0003	0.0000 ± 0.0000	0.0012 ± 0.0000	0.0809 ± 0.0029	0.0116 ± 0.0004	0.99	218 ± 14	74 ± 3	79 ± 3
5	0.0511 ± 0.0002	0.0000 ± 0.0000	0.0012 ± 0.0000	0.0680 ± 0.0024	0.0096 ± 0.0003	0.99	245 ± 9	62 ± 2	67 ± 2
6	0.0522 ± 0.0002	0.0000 ± 0.0000	0.0013 ± 0.0000	0.0653 ± 0.0023	0.0091 ± 0.0003	0.99	294 ± 9	58 ± 2	64 ± 2
7	0.0522 ± 0.0002	0.0000 ± 0.0000	0.0013 ± 0.0000	0.0654 ± 0.0024	0.0091 ± 0.0003	0.99	294 ± 11	58 ± 2	64 ± 2

and 47-3), and the second group ranging from 0 and 20 Ma corresponds to the Si-richest zones (samples 90-20, 47-5, 47-4 and 47-11). A few older chemical ages (120–140 Ma) have been obtained from the Si-rich and Ca-poor pitchblendes in sample 47-11. In the RZ and WGZ samples, the whole rock U contents are lower and the effects of the presence of relics of primary lead from the dissolution of hydrothermal uranium oxides (mainly incorporated in radiogenic galena) affect largely the Pb/U ratios, which are thus not usable for age estimation, but are clear indicators of element transfer.

Discussion

Mineralogical and geochemical impacts of U redox fronts

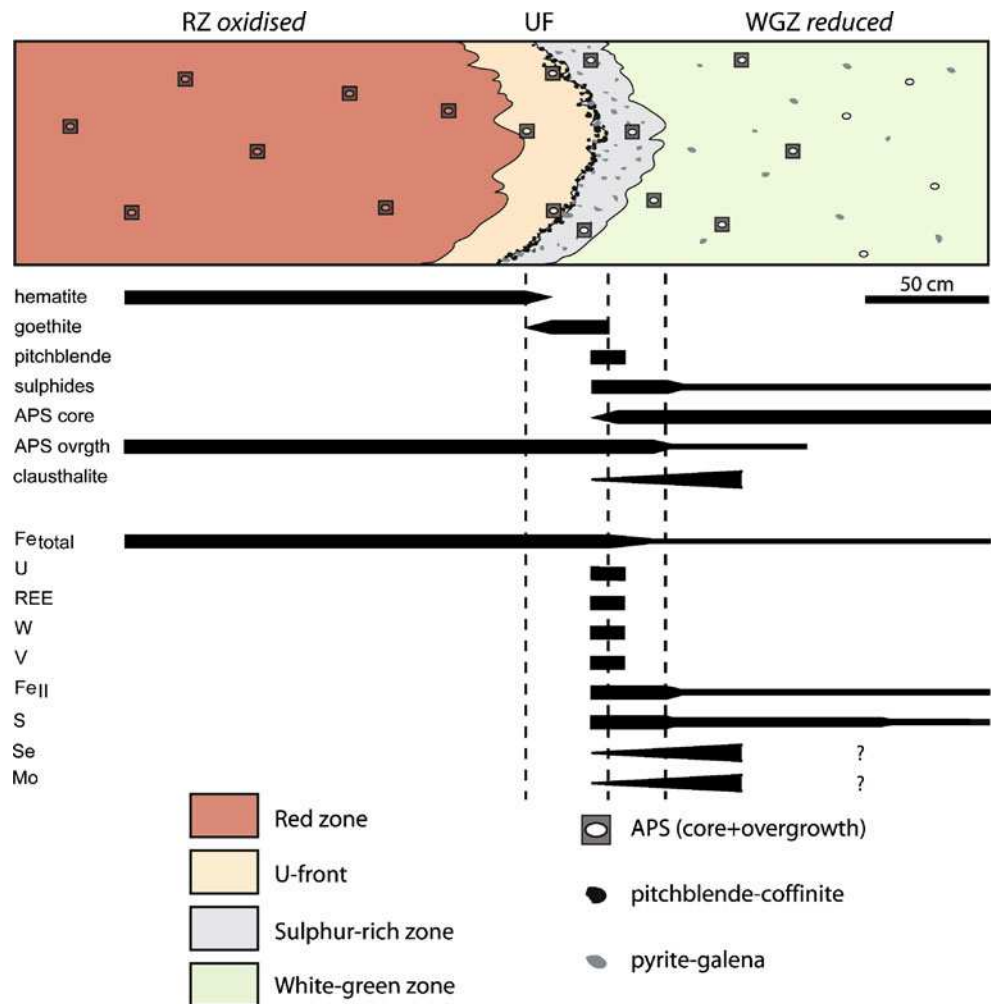
The meteoric-related redox fronts developed in the basement below the Athabasca Basin are composed of three distinct zones (Fig. 14):

- A reduced white-green zone, mainly composed of an early, hydrothermal clay-mineral paragenesis (illite–sudaite), coeval with the primary hydrothermal unconformity-related U mineralisation (1.3–1.6 Ga);

	White-green zone	U front	Red zone
primary minerals			
quartz I			
zircon			
monazite			
apatite			
chlorite			
phengite			
TiO ₂			
hydrothermal alteration stage			
illite			
sudaite			
dravite			
I/S			
APS core			
quartz II			
pyrite			
galena I			
U redox front			
pitchblende			
goethite			
hematite			
APS rim			
coffinite			
pyrite II			
galena II			
clausenthalite			
kaolinite			

Fig. 14 Simplified paragenesis and mineralogy for the studied uranium redox front samples of Eagle Point and P-Patch deposits. The observed minerals were classified in three categories (primary minerals, hydrothermal alteration stage and U redox front). *Primary minerals* correspond to metamorphic and magmatic minerals, *hydrothermal alteration stage minerals* correspond to those developed during unconformity-related deposit formation, and *U redox front minerals* includes those crystallising during uranium roll-front development. *Kaolinite* corresponds to the kaolinite-rich zone development after U roll-front formation

Fig. 15 Schematic sketch of a uranium redox front developed in the basement of the Athabasca Basin. The mineralogy, the mineral content, distribution of associated redox sensitive elements in each zone (red zone, uranium front, sulphur-rich zone and white-green zone) are indicated



- A uranium front characterised by U oxides, goethite, sulphides and Sr–SO₄-rich APS, impregnating the clay-rich matrix; and
- A red oxidised zone, corresponding to the fluid pathway, characterised by a high hematite and Sr–SO₄-rich APS content.

The main mineralogical modifications in the UF compared to WGZ correspond to the crystallisation of Fe oxides (hematite) and hydroxides (goethite), U oxides (pitchblende), sulphides and APS overgrowths (LREE-poor), whereas all other minerals inherited from the early history are unaltered. Pyrite and galena were dissolved from the RZ, but are abundant in the UF and even more abundant in the WGZ beyond the UF (sulphur-rich zone). Pitchblende is mainly associated with the sulphides, but also coats Ti oxides and zircons. LREE-depleted APS overgrowths are developed around early crystallised LREE-rich APS crystals in the UF and the WGF close to UF. In the UF and RZ, the LREE-rich cores are partially to totally dissolved. Se-bearing minerals (e.g.

clausthalite) also occur in the UF and WGZ. Euhedral grains of galena (Gn₂) crystallised after pitchblende in the UF, and some occur in dissolution cavities. Coffinitisation of pitchblende resulted in Pb loss and possibly the late galena crystallisation. Therefore, the formation of meteoric-related redox fronts within the hydrothermal alteration haloes of unconformity-related U deposits was associated with profound modification of the mineral paragenesis linked to unconformity-related uranium deposit formation (Fig. 15).

U, Fe, Ca, Pb, LREE, V, Y, W, S, Mo and Se were the main mobile elements during mineralogical changes linked to the formation of the U redox fronts. The spatial distribution of these elements across the redox front reflects the aforementioned mineralogical changes (U, V, S, Fe²⁺ more abundant in the UF, Fe³⁺ in the RZ and Mo in the WGZ, except Se which shows a more complex behaviour; Fig. 15). The main elemental enrichments in the UF and RF are between ten to hundred times greater than the hydrothermal alteration halo contents and are particularly high for U, REE, W and Fe.

Comparison with the known uranium meteoric-related redox front occurrences

Roll-front U deposits have been extensively studied in silicoclastic contexts, especially in the USA (Fischer 1950; Shawe and Granger 1965; Adler 1974; Granger and Warren 1969; Harshman 1974; Goldhaber et al. 1978 among others), Kazakhstan (Jaireth et al. 2008 and references therein), China (Min et al. 2005, 2007; Cai et al. 2007 among others) and Australia (Jaireth et al. 2008). Similar U roll-fronts have been also described in granite-hosted U-mineralised episyenites in the French Massif Central (Cathelineau 1982; Respaut et al. 1991) where Permian U ores are altered and mobilised along roll-fronts related to downward percolation of meteoric water along the clay-rich episyenite pipes. These U roll-fronts are all characterised by a strong colour contrast between the oxidised and reduced zones on either side of the U front, directly reflecting the mineralogical composition and the redox state of the two zones. The mineralogical and geochemical patterns described in the literature within basin and basement-hosted roll-fronts are comparable to those in the Athabasca basement for the redox fronts presently studied with a significant mobility of U, Fe, V, S, Se, Pb and Mo and similar mineralogy consisting of U oxides, sulphides and goethite–hematite (c.f. Granger and Warren 1969; Harshman 1974; Cathelineau 1982). However, native Se, ferroselite or jordisite, related to meteoric processes and observed in other roll-front uranium deposits, have not been observed in the Athabasca basement despite significant Mo (up to 908 ppm), and to a lesser extent, Se anomalies (up to 34.4 ppm) in the WGZ. This may be due to the small grain size of the Mo and Se minerals or the limited size of the samples.

Although geological contexts of sandstone-hosted and basement-hosted roll-fronts differ greatly (i.e. host rocks, permeability and source of elements), both types present unambiguously similar characteristics, indicating comparable genetic conditions. The roll-fronts of the French Massif Central have the closest similarities with the Athabasca redox fronts because they are developed in previously hydrothermally altered and U-mineralised crystalline rocks and are associated with a late kaolinisation episode. The presence of a well-developed early hydrothermal alteration halo appears to be a prerequisite for meteoric-related U redox front formation in basement rocks through increases in rock permeability favouring large-scale fluid infiltration and element dispersion in large clay-rich pipes. Nevertheless, the lower permeability of altered basement rocks compared to sedimentary rocks limits the development, the size, element zonation and geometry of the redox front compared to classic roll-front deposits, these differences precluding them being regarded as *sensu stricto* roll-front despite they share many roll-front characteristics.

Physicochemical conditions (fluid composition, temperature, pH and oxido-reduction) of meteoric-related redox front formation

The roll-front U ore deposits in New Mexico, Wyoming and Texas (USA) are the result of downward percolations of low-temperature oxidising meteoric solutions through the porous and permeable host rock (Shawe and Granger 1965; Granger and Warren 1969). In the Athabasca Basin, the percolation of oxidised fluids, through the reduced lithologies of the primary hydrothermal alteration halo, during the formation of the redox fronts is indicated by the crystallisation of goethite, hematite and sulphate–strontium-rich overgrowths (svanbergite) on earlier goyazite cores. Goethite crystallisation in the UF of the studied deposits, and for the majority of known U roll-fronts, also indicates low-temperature conditions, probably lower than 50°C, as shown by the thermodynamic calculations which demonstrated that goethite is stable in the roll-front formation conditions only below 50°C (Trolard and Tardy 1987; Dubessy et al. 1999).

P/S and LREE contents of APS minerals can be considered as markers of the relative variations of pH and fO_2 during the geological evolution of the basement (Gaboreau et al. 2007). According to Komninou and Sverjensky (1996) and Gaboreau et al. (2005), the high contents of P and LREE in APS cores document a pH increase and the presence of reducing conditions corresponding to hydrothermal alteration during unconformity-related deposit formation. Accordingly, APS overgrowths, which display low P/S ratios, are consistent with oxidising conditions during U redox front formation (Fig. 9). During progression of the redox front and development of oxidising conditions, the LREE-rich cores were dissolved, whereas S-rich overgrowths crystallise in the vicinity of UF and were stable in the RZ. Therefore, the presence of APS minerals with chemically contrasting zones (core and overgrowth) in the vicinity of the U redox front confirms the existence of clear contrasting redox conditions (reduced for core crystallisation and oxidised for overgrowth crystallisation) at the same place but at different times (unconformity-related ores for core crystallisation and meteoric-related redox front formation for overgrowth crystallisation).

The distribution of most elements within different zones of the redox fronts (RZ, UF and WGZ) in the Athabasca basement reflects the variation of the redox conditions during the influx of meteoric fluids and the relative redox potential of each of the elements, as described for the other U redox front deposits such as roll-front deposits. At the redox interface (oxidised edge of the UF), pyrite, APS LREE-rich cores and U oxides were essentially dissolved. Beyond the redox interface, sulphides, sulphates (APS overgrowths) and U were redeposited. Sulphur from pyrite

and galena dissolved during the oxidation of the primary reduced lithology was redeposited in the UF and also beyond it as pyrite, native S, sulphates and/or jordisite. As a result, a small zone, richer in pyrite than the reduced zone, formed beyond the UF. Solutions migrating towards the early hydrothermal alteration halo encountered progressively more reducing conditions. Consequently, an elemental zonation developed with the more readily reduced species up-dip (e.g. Se) and the less readily reduced species down-dip (e.g. Mo).

In light of the mineralogical and geochemical similarities, the same genetic processes are proposed for the formation of meteoric-related redox fronts in the Athabasca Basin basement and for classical U roll-fronts: that is, the reduction of dilute, oxygenated, U-bearing fluids as they infiltrated permeable reduced lithologies. The observed redox fronts therefore have no genetic to the early unconformity-related U ores associated with circulation of hotter basinal brines (Derome et al. 2005; Richard et al. 2010). Several reduction mechanisms have been proposed in the U roll-fronts, including reactions with Fe-bearing minerals (Fe oxides, sulphides; Granger and Warren 1969; Adler 1974; Cathelineau 1982), carbonaceous matter (Reynolds et al. 1982; Spirakis 1996), petroleum and H₂S (Adler 1974; Curiale et al. 1983; Jaireth et al. 2008) or microbial actions (Min et al. 2005; Cai et al. 2007). In the redox fronts of the Athabasca basement, Fe and S, which were initially concentrated in pyrite and galena, can be considered as the main reductants for U, V, Mo, and Se deposition, as proposed for basement-hosted U roll-fronts of French Massif Central (Cathelineau 1982).

Source of U and REE in the Athabasca basement redox fronts

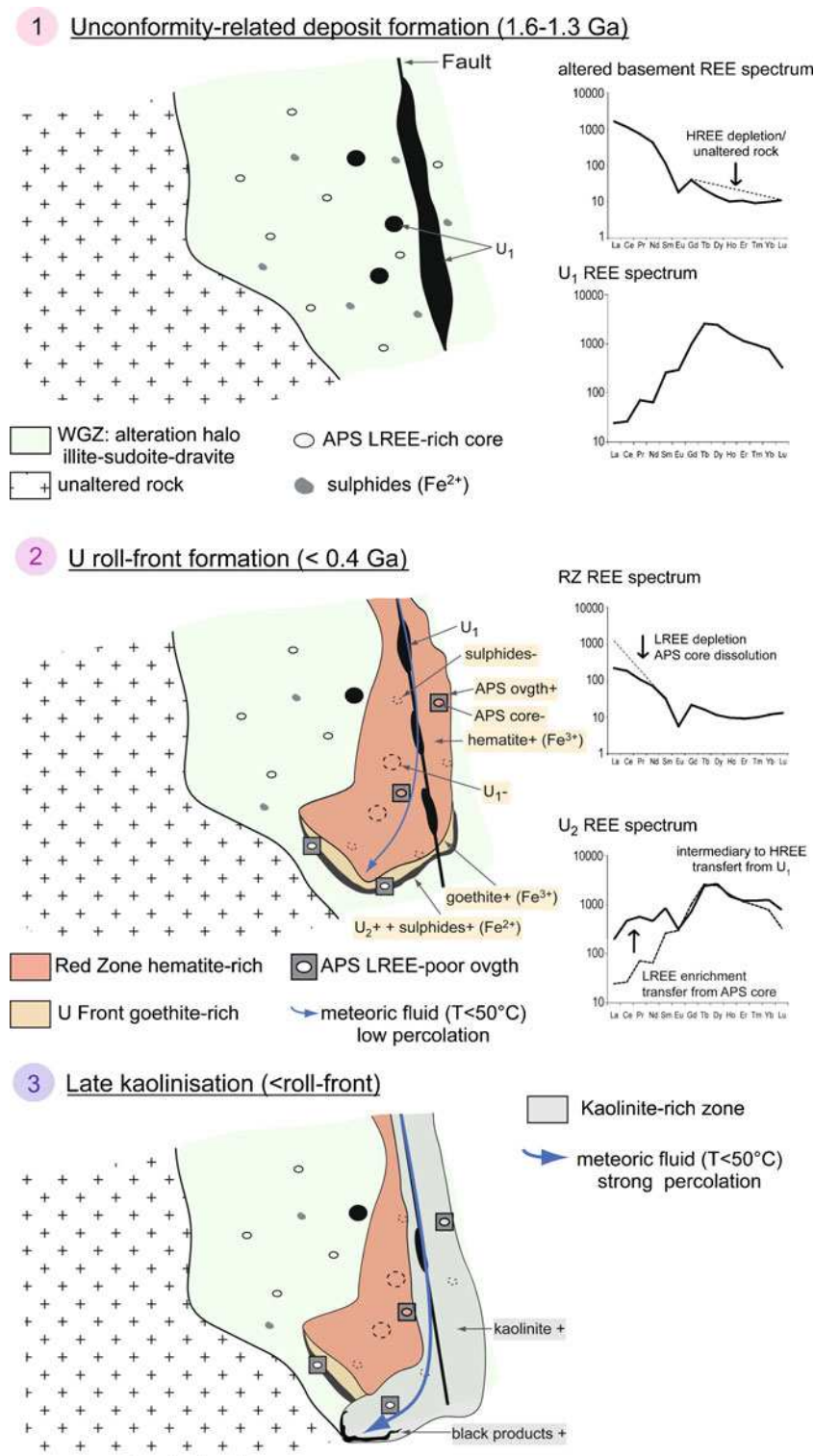
The chondrite-normalised REE patterns for the U oxide minerals of unconformity-related Eagle Point deposit have bell-shaped patterns (Fig. 8) with lower normalised abundances of LREE and HREE, typical of the unconformity-related deposits of the Athabasca and Kombolgie (Australia) basins (Pagel et al. 1987; Fryer and Taylor 1987; Fayek and Kyser 1997; Bonhoure et al. 2007; Mercadier 2008). The U oxides of the P-Patch and Eagle Point meteoric-related redox fronts also exhibit bell-shaped patterns, but LREE are up to one thousand times more enriched compared to classical unconformity-related U oxides. The REE patterns for redox front U oxides are inherited from the dissolution of precursor phases, with a combination of the bell-shaped REE distribution from the primary U oxides from diagenetic–hydrothermal ores and LREE from the dissolution of LREE-rich APS cores (Fig. 16). The low temperature (<50°C) of the fluid and its composition (meteoric-derived), with low concentrations of complexing anions, would not have

induced any significant fractionation of the REE from the precursor phases during this event, the stability of the REE patterns indicating that the fluids were weakly complexing, as is generally the case for meteoric fluids (Luo and Byrne 2001). More refractory, minor REE-bearing accessory minerals (zircon or apatite) were not altered by the meteoric fluid, and thus, their REE composition does not affect the REE pattern of UF mineralisation. LREE enrichments were previously described from whole rock analysis of uranium oxides (Fayek and Kyser 1997) and ion microprobe analysis (Bonhoure et al. 2007) for young mineralisation (as evidenced by the low U/Pb ratios or chemical ages) in the Athabasca Basin. Bonhoure et al. (2007) interpreted these changes as the result of late enrichments by alteration of unconformity-related U oxides with bell-shaped patterns. The present study suggests that the strong LREE enrichment of the U oxides previously observed was related to the formation of late U redox fronts. One of the fundamental characteristics of meteoric-related redox front formation in the Athabasca basement, as with the roll-fronts of the Massif Central (Cathelineau 1982), is the existence of older U mineralisation, which acted as a major source of elements mobilised by meteoric-derived fluid. The range of whole rock chemical ages of the RZ and WGZ tends to support such an origin (Fig. 13). When no U contamination from the UF is present, these ages are older than redox front formation (<0.4 Ga) than unconformity-related U deposit formation (1.3–1.6 Ga) and sometimes even older than the crystallisation age of the protolith. These unrealistic ages result from excess of Pb, probably of radiogenic origin, derived from the dissolution of unconformity-related U oxides during meteoric-derived fluid circulation. These observations confirm the existence of massive fluid circulations after unconformity-related deposit formation until recent times with differential mobility of radiogenic Pb and U (Kister et al. 2004).

Temporal and geodynamic conditions of redox front formation

²⁰⁷Pb/²⁰⁶Pb ages of uranium oxides in one meteoric-related U redox front in the Eagle Point deposit range from 294 to 147 Ma, confirmed by the chemical ages (89–325 Ma) obtained from whole rock U–Pb–Th contents for the UF of the Eagle Point and P-Patch deposits. Although major remobilisation of the U deposits have already been considered in the Athabasca Basin (Hoeve and Quirt 1984; Kotzer and Kyser 1995; Kister et al. 2004), the existence of U redox fronts developed during the 400–0 Ma period has not been previously recognised. The initiation of the remobilisation process at ca. 400–250 Ma is interpreted to be related to basin uplift rather than a regional- or

Fig. 16 Schematic representation of the U redox front formation and kaolinite-rich zone development in the U basement-hosted deposits of the Athabasca Basin. 1 Mineralogy in the U basement-hosted deposits after the deposition of the hydrothermal mineralisations (U_1 , ca. 1.6–1.3 Ga). The alteration halo around the mineralisation, formed by the percolation of basinal brines, is mainly composed of an illite-sudoite $\pm$ dravite matrix. APS, the main LREE-bearing mineral, are formed with a LREE-rich core. Sulphides, mainly pyrite and galena, are disseminated in the clay-rich matrix. The REE spectrum of the hydrothermal halo is characterised by a HREE depletion (compared to unaltered rock) linked to accessory mineral alteration. The REE spectrum of U_1 is typical of unconformity-related deposits with a bell-shaped pattern. 2 Development of the U redox fronts within the hydrothermal halo (<0.4 Ga). The percolation of a cold ($T < 50^\circ\text{C}$) and oxidising meteoric-derived fluid favours the remobilisation of U_1 , the dissolution of sulphides and LREE-rich APS core and the redistribution of the elements in the Red zone and U front of the roll-fronts. Iron from sulphides is redistributed in hematite (hematite+) and goethite (goethite+). S from sulphides is redistributed in the sulphide-rich zone and in LREE-depleted APS overgrowths (APS ovgrth+). LREE from APS cores and intermediary-to-HREE from U_1 are transfer to U_2 . 3 Late kaolinisation ($<\text{roll-front}$). The renewed percolation of meteoric-derived fluids leads to the development of a kaolinite-rich zone crosscutting the U redox fronts. The preexisting mineral assemblage is destabilised and replaced by a kaolinite-rich matrix, the uranium being redistributed as black products (i.e. sooty pitchblende)



continental-scale tectonic event. The decompression associated with the uplift could have reopened some of the preexisting faults, allowing the infiltration of cold oxidising meteoric-derived fluids into the basement, along highly permeable zones. The paleolatitude of the Laurentia megacontinent, between Early Devonian (390 Ma) and

Late Carboniferous (306 Ma) times, indicates that the Athabasca Basin was probably located close to the Equator (Scotese 1997; Keppie 2004; Bozkurt et al. 2008). Such latitudes are characterised by abundant precipitation and are highly favourable to the formation of lateritic profiles, with the formation of hematite, goethite and kaolinite (Fritz

1975; Tardy and Nahon 1985; Ramanaidou et al. 1996). Although the sensu stricto lateritic mechanisms cannot be proposed for the U redox front formation due to the depth of the studied features (tens to hundreds of metres below the ground at the moment of their formation), the hydrogeologic regime at the Equator, with the massive circulation of meteoric fluid, can be related to the formation of U redox fronts and subsequent kaolinisation episode (see next section). Moreover, the U/Pb chemical ages obtained from whole rocks and U oxides and isotopic U–Pb data indicate either multiple episodes or a nearly continuous migration of U and Pb through the redox front until very recent times.

Post U redox front kaolinisation

Kaolinite-rich structures commonly crosscut the meteoric-related U redox fronts, with destabilisation of the paragenesis associated with unconformity-related and redox front mineralisation and the formation of a kaolinite-rich matrix (Figs. 1 and 6). Macroscopically, kaolinite-rich structures are characterised by a dissemination of sooty pitchblende (black products), sourced from the destabilisation of the redox front U oxides, within a kaolinite-rich matrix, although the association of kaolinite and sooty pitchblende could indicate a synchronous formation of kaolinite with the U oxide of the redox fronts (Fig. 5e). The chemical compositions of these U oxides (especially low Pb contents) indicate young crystallisation age during post-kaolinisation events.

Intense kaolinisation associated with percolation of meteoric fluid with a temperature lower than 50°C (H and O isotopic studies) has been described in the Athabasca Basin (Halter et al. 1987; Wilson and Kyser 1987; Kotzer and Kyser 1995). For example, kaolinisation associated with fault zones in the illite–chlorite alteration halo of Key Lake and McArthur River deposits was interpreted to have been related to Post-Cretaceous meteoric water circulations (Kotzer and Kyser 1995). The characteristics of this event have been only determined by isotopic analysis of clay minerals, and the physicochemical conditions of the percolation of meteoric waters have not been precisely constrained. The low temperatures estimated from stable isotope systematics are in good agreement with those proposed here for the development of late kaolinisation in Athabasca Basin or invoked in the French Massif Central (Cathelineau 1982). Indeed, kaolinite is the last mineral to be formed during the evolution of the system and is thus supposed to have crystallised at lower temperature than goethite, which is overprinted by the kaolinite alteration.

The temporal succession of U redox front development and kaolinisation may have been linked to the initial conditions of the fluid circulation system following basin

uplift (Fritz 1975). Percolation of meteoric-derived fluid in basement faults and permeable altered zones (mainly hydrothermal alteration halo) may have occurred in a relatively closed system in which the fluids circulated slowly and were not often recharged (Fig. 16). Diffusive processes may have been dominant in the clay-rich zones, and these restrictive fluid percolation conditions would have favoured the formation of the U redox fronts. The hydrologic regime, balanced among factors such as climate and host rock properties, may have determined whether such ores formed (Granger and Warren 1969). During ongoing erosion and uplift of the basin, the associated decompression may have become linked to fault reopening and massive meteoric-derived fluid influx into the basement. These new conditions, which favoured oxidising fluid recharge and substantial fluid percolation, generated massive kaolinisation by destruction of previous minerals (hydrothermal- and redox front-related). The U redox front and kaolinisation episodes were thus generated by similar meteoric-derived fluids, but with contrasting fluid regimes due to the progressive opening of fractures during basin uplift. The fluid temperature (<50°C) indicates that the thickness of the Athabasca Basin during the 390–300 Ma period in the vicinity of the Eagle Point and P-Patch deposits was <2 km based on a normal geothermal gradient (30°C/km).

Impact of remobilisation on hydrothermal unconformity-related deposits

The sampling performed for the present study at the P-Patch and Eagle Point basement-hosted deposits, at core and mine scales, indicates that the majority of the intercepted U mineralisation is distributed as redox front systems within the hydrothermal alteration halo and that the hydrothermal U oxides are a minor component. For example, at the P-Patch deposit, meteoric-related U redox fronts correspond to approximately 80% of the mineralised intercepts observed in drill holes. Moreover, this redox front mineralisation has been observed in other basement-hosted deposits within the Athabasca Basin (Millennium deposit, Mercadier 2008) and in several unconformity-associated ores such as at Shea Creek, McArthur or Cigar Lake (Cumming and Krstic 1992; Philippe et al. 1993; Cuney et al. 2002; Kister 2003; Bonhoure et al. 2007) where U is mainly concentrated at the unconformity or in the sedimentary strata. For example, a U/Pb upper intercept age of 391 ± 34 Ma (Cuney et al. 2002) and a similar chondrite-normalised REE pattern to redox front U oxides (Bonhoure et al. 2007) were obtained from late pitchblende in the Shea Creek deposit. The massive impact of meteoric fluid influx during the 400–250 Ma period on the unconformity-related deposits of the Athabasca Basin is also

marked by the general radiogenic Pb losses observed in the primary hydrothermal U oxides. For example, the lower intercept ages on U–Pb Concordia for several unconformity-related U oxides in the main deposits, summarised in Table 7, are in the 400–250 Ma period. The present study provides further evidence that late meteoric fluid circulations in the Athabasca Basin and basement had a major imprint on the unconformity-related deposits, strongly modifying the mineralogy, chemistry and U distribution (Fig. 16).

Contribution on the understanding of unconformity-related U deposits

The results of this study have several key implications for the understanding of the Athabasca Basin U deposits. Firstly, young meteoric-related redox front related to young U mineralisation has been described in detail for the first time. The typical petrographic, mineralogical, isotopic and geochemical characteristics of these redox fronts provide tools to distinguish mineral assemblages of primary and remobilised mineralisations. Hence, the hematized and kaolinite-rich zones observed in unconformity-related deposits have to be carefully reconsidered to determine which are primary ore depositions and which result from later infiltration of meteoric fluids. These results further emphasise the crucial importance of the identification of the reducing mechanisms involved in the genesis of the primary ores, which are not yet clearly understood. Secondly, meteoric fluid influx in the Athabasca Basin is temporally constrained to a period between 400 Ma and the current time, and their importance on the current distribution of the U resource is emphasised. Thirdly, the REE patterns of uranium oxides in this type of U deposit where multiple phases of fluid percolation and remobilisation occurred appear to provide a meaningful tool in facilitating discrimination of each mineralisation type and therefore help in their interpretation of their relative importance.

Conclusion

This study provides the first description of a new type of U mineralisation in the basement rocks of the Athabasca Basin, namely the meteoric-related redox front mineralisations. These remobilised U oxides represent a very common feature within Athabasca unconformity-related deposits and explain some important mineralogical and geochemical characteristics. The sampling for the present study at the P-Patch and Eagle Point deposits, at both core and mine scales, indicates that the majority of the intercepted U mineralisation is distributed as meteoric-related redox front systems within the hydrothermal alteration halo, whereas hydrothermal U oxides make a subordinate contribution to the ores. The meteoric-related U redox front mineralisation is characterised by distinct mineralogical and geochemical signatures and a young age (<400 Ma) compared to the early hydrothermal unconformity-related mineralisation. Moreover, this redox front mineralisation has been observed at other major U deposits in the Athabasca Basin, demonstrating that these processes had a large imprint in the unconformity-related deposits throughout the Athabasca Basin.

The Athabasca basin meteoric-related redox fronts share most of the characteristics of those already described in sedimentary or basement environments, suggesting that all the meteoric-related fronts, although developed in variable geological settings and at different times, formed under similar physical and chemical conditions.

The present study confirms the past existence of massive meteoric-derived fluid circulation systems as previously described in the Athabasca Basin, but emphasises their impact on the redistribution of the U ores and the succession of events that affected them (U redox fronts followed by kaolinisation). These processes were responsible for the observed mineralogy and geochemistry in a large part of the ores in unconformity-related U deposits.

Table 7 Summary of published isotopic U–Pb ages (upper and lower intercepts) of primary unconformity-related uranium oxides from several Athabasca Basin uranium deposits

Deposit	Reference	Upper intercept (Ma)	Lower intercept
Cigar Lake	Philippe et al. (1993)	1,341±17	328±30
	Fayek et al. (2000)	1,467±63	443±96
	Fayek et al. (2002a)	1,481±47	437±73
Sue Zone	Fayek et al. (2002b)	1,486±9	458±18
Key Lake	Cumming and Krstic (1992)	1,329±17	231±31
Midwest	Cumming and Krstic (1992)	1,331±13	334±36
Dawn Lake	Cumming and Krstic (1992)	1,349±15	415±37
Shea Creek	Kister (2003)	1,275±23	433±26
Millennium	Cloutier et al. (2009)	1,278±200	80±370

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