

Brine–rock interaction in the Athabasca basement (McArthur River U deposit, Canada): consequences for fluid chemistry and uranium uptake

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ABSTRACT

The nature of uranium source rocks, transport conditions and deposition processes are still highly controversial for world-class unconformity-related U deposits. This article presents the first detailed chemistry of brines associated with the giant McArthur River U deposit, Canada. LA-ICP-MS analysis of individual fluid inclusions suggests mixing between a Na–Ca–Mg–K–Sr–Ba brine and a Ca–Mg–Na–K–Sr–Ba brine. The brines share a common origin (evaporated seawater) and show evidence for contrasting interaction with basement rocks. The

Na-rich brine lost Mg and K in alteration haloes around U ores, while the Ca-rich brine results from Na–Ca exchange and Sr–Ba gain. U concentrations ($0.3\text{--}530\text{ }\mu\text{g g}^{-1}$) are anomalously high compared with usual basinal fluids, this indicating that U uptake occurred within basement rocks. The two brine end-members have mixed within the main U deposit area, which could be one of the major driving forces for U deposition.

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Introduction

The McArthur River deposit is one of the largest U deposits in the world (c. 200 000 t U_3O_8 at 25% average) and is of the unconformity-related type (Kotzer and Kyser, 1995; Derome *et al.*, 2005). Basinal brines are thought to have been involved in the alteration and mineralising processes that occurred at the interface between the middle Proterozoic Athabasca Basin and the Archaean to lower Proterozoic basement (Hoeve and Sibbald, 1978; Pagel *et al.*, 1980). These brines are believed to have circulated at the basement–cover interface and strongly interacted with various lithologies, leading to the formation of large illite–sudaite–dravite alteration haloes around U ores (Wilson and Kyser, 1987; Kotzer and Kyser, 1995; Fayek and Kyser, 1997; Renac *et al.*, 2002; Alexandre *et al.*, 2005).

The chemical composition of the brines was estimated in the H_2O – NaCl – CaCl_2 $\pm$ MgCl_2 system by Derome *et al.* (2005) based on microthermometry, Raman spectroscopy and laser-induced breakdown spectro-

scopy (LIBS) analysis of individual fluid inclusions. This study revealed mixing between a NaCl-rich brine (25 wt% NaCl, up to 14 wt% CaCl_2 and up to 1 wt% MgCl_2) and a CaCl_2 -rich brine (5–8 wt% NaCl, 20 wt% CaCl_2 and up to 11 wt% MgCl_2) at the time of ore deposition. However, a more comprehensive survey of the brine chemistry is needed to characterise better the mixing and to identify markers of the fluid–rock interactions. In addition, the determination of U concentrations in brines was one of the main objectives of the study.

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is presently one of the best techniques for the determination of major and trace element concentrations in individual fluid inclusions (Günther *et al.*, 1998; Heinrich *et al.*, 2003). Furthermore, this technique has enabled the successful determination of the U content of individual fluid inclusions related to the magmatic–hydrothermal activity of various granitic plutons (e.g. Audétat *et al.*, 2000; Audétat and Pettke, 2003; Zajacz *et al.*, 2008) and demonstrated that such high temperature–high chlorinity magmatic brines are able to carry up to $15\text{ }\mu\text{g g}^{-1}$ U.

The results of the first LA-ICP-MS analyses of fluid inclusions from the richest U deposit in the world are reported in this article. This study

is the first attempt, after the pioneering work by Philippot *et al.* (2000), to determine the U concentration in U-mineralising fluids. The McArthur River U deposit was selected because a detailed fluid inclusion study by Derome *et al.* (2005) provided a full description of the fluid events associated with high-grade U mineralisation.

Geology and sampling

The McArthur River deposit is located in the eastern part of the Athabasca Basin, Saskatchewan, Canada. Uranium mineralisation is mostly basement-hosted, but straddles the unconformity and is structurally controlled by a major reverse fault. The main alteration assemblage comprises coarse-grained illite, Mg-chlorite (sudaite) and Mg-tourmaline (dravite) associated with minor amounts of pyrite, chalcopyrite and quartz (McGill *et al.*, 1993; Kotzer and Kyser, 1995; Derome *et al.*, 2005). U–Pb geochronology determinations on the oldest U oxide generation yielded mineralisation ages of 1514 ± 18 Ma (Cumming and Krstic, 1992), 1519 ± 22 Ma (Fayek *et al.*, 2002) and 1540 ± 19 Ma (Alexandre *et al.*, 2009a) respectively.

The following successive generations of authigenic quartz are represented around the McArthur River U

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ores: (i) quartz overgrowths (Qz1) in sandstones with small and scarce NaCl-rich brine inclusions, (ii) pervasive silicification (Qz2) in sandstones with small and scarce CaCl₂-rich brine inclusions, (iii) euhedral quartz (Qz3) surrounded by UO₂ in ores occurring in sandstones, with large and abundant NaCl-rich brine and CaCl₂-rich brine inclusions and (iv) euhedral quartz (Qz4) cementing UO₂ in sandstones and basement ores, containing large and abundant NaCl-rich brine and CaCl₂-rich brine inclusions (see the detailed description in Derome *et al.*, 2005). Qz3 and Qz4 are considered as subsynchronous with the U deposition. Mixing between the NaCl-rich and CaCl₂-rich brines was indicated in Qz3 and Qz4. With the goal of establishing the detailed compositions of the NaCl-rich and CaCl₂-rich brine end-members and their mixing terms, fluid inclusions in Qz3 and Qz4 were the best candidates for microthermometry and LA-ICP-MS analysis (Fig. 1).

Analytical methods

Microthermometry was carried out on fluid inclusions from Qz3 and Qz4 using a Linkam MDS600 heating-cooling stage. The observed temperatures of phase changes are the following: eutectic melting (T_e), ice melting [$T_m(\text{ice})$], hydrohalite melting [$T_m(\text{hyd})$], halite dissolution [$T_s(\text{NaCl})$] and total homogenisation (T_h). According to the calibration curves, the temperatures of phase changes are given with an accuracy of about $\pm 5^\circ\text{C}$ for T_e , $\pm 0.1^\circ\text{C}$ for

$T_m(\text{ice})$ and $T_m(\text{hyd})$, and $\pm 1^\circ\text{C}$ for $T_s(\text{NaCl})$ and T_h .

Forty-five fluid inclusions were analysed using a 193-nm ArF excimer laser (Lambda Physik, Göttingen, Germany) combined with an ELAN 6100 DRC ICP-MS (Perkin Elmer, Woodbridge, Canada), at the ETH Zürich, Switzerland, under instrument conditions similar to those reported in Pettke *et al.* (2004). The procedure for reconstituting the fluid inclusions' absolute element concentrations can be found in Heinrich *et al.* (2003). Briefly, ^7Li , ^{11}B , ^{23}Na , ^{24}Mg , ^{31}P , ^{39}K , ^{40}Ca , ^{55}Mn , ^{56}Fe , ^{59}Co , ^{65}Cu , ^{66}Zn , ^{85}Rb , ^{88}Sr , ^{133}Cs , ^{137}Ba , ^{208}Pb and ^{238}U were recorded. Transient LA-ICP-MS signals for Si, Na, Ca, Mg, K and U for one U-rich inclusion are shown in Fig. 2. After correction for the host quartz signal contribution, the resulting fluid element count rates were converted into element concentration ratios using calibrations with SRM610 glass from NIST. Absolute element concentrations were then calculated based on Na as the internal standard using microthermometric equivalent NaCl data corrected for the presence of other major salts [e.g. MgCl₂, (Ca–Mg)Cl₂]. Limits of detection (LODs) were calculated using the 3σ criterion (Longerich *et al.*, 1996).

Na–Ca–Mg relationship

Fluid inclusions were classified according to the nomenclature of the deposit already published (Derome *et al.*, 2005). Inclusions showing $T_m(\text{hyd})$ higher than $T_m(\text{ice})$ are referred to as Lw2 inclusions. Inclusions showing $T_m(\text{ice})$ below -30°C or showing failure in freezing even down to -190°C are referred to as Lw' inclusions, and inclusions similar to Lw' inclusions showing a halite cube at room temperature are referred to as Lwh' inclusions. The estimated bulk salinities range from 26.9 to 29.2 eq. wt% NaCl for Lw2 inclusions and from 28 to 35 eq. wt% NaCl for Lw' and Lwh' inclusions. The three fluid-inclusion types were found in the same samples. All studied fluid inclusions are considered primary or pseudo-secondary and thus contemporaneous with the growth of their host quartz.

The main characteristics of fluid inclusions from the McArthur River deposit are summarised in Table 1. On the basis of Na/Ca and Ca/Mg ratios measured by LIBS on individual inclusions, Derome *et al.* (2005) reported that Lw2 inclusions are representative of the NaCl-rich brine, while the Lw' and Lwh' inclusions are more typical of the CaCl₂-rich brine. Although fluid inclusions were

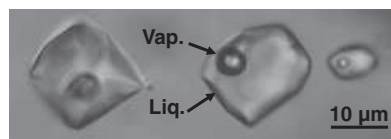


Fig. 1 Typical U-bearing fluid inclusions in quartz cementing UO₂ (Qz4) analysed by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) (an example of a transient LA-ICP-MS signal is shown in Fig. 2). Liq.: liquid phase. Vap.: vapour phase. See Derome *et al.* (2005) for a detailed description of fluid inclusions from the McArthur River deposit.

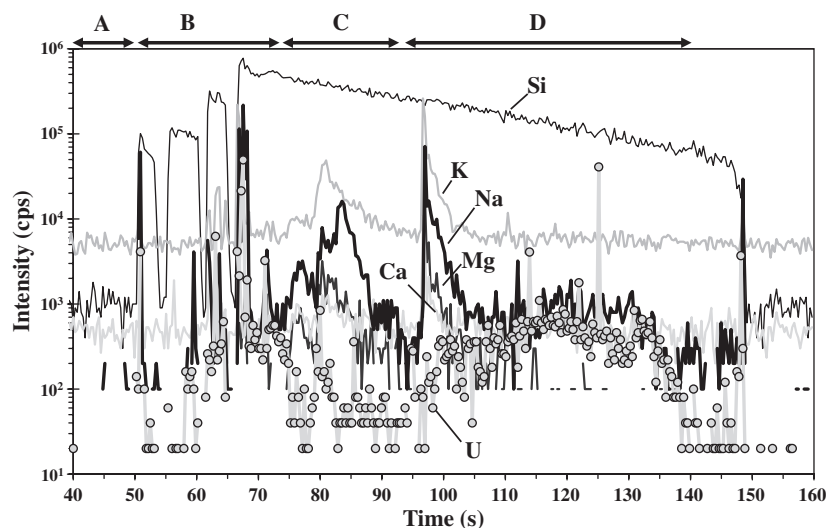


Fig. 2 Transient LA-ICP-MS signal of a U-bearing fluid inclusion, with signal count rates for Si, Na, Ca, Mg, K and U, shown on a logarithmic scale. (A) Background. (B) Stepwise widening of the beam size, as monitored by Si. U is smeared on the surface of the quartz chip. (C) Signal of a small inclusion, drilled through before the targeted inclusion was hit (not used for quantification). (D) Signal of a $530\text{ }\mu\text{g g}^{-1}$ U inclusion. Note that U and Na are well correlated.

Table 1 Summary of the characteristics of the Lw2, Lw' and Lwh' type fluid inclusions at McArthur River, after Derome *et al.* (2005). All data are based on microthermometry, LIBS and Raman spectroscopy.

	NaCl-rich brine	CaCl ₂ -rich brine	
Type	Lw2	Lw'	Lwh'
<i>T_e</i> (°C)	–75 to –50	–75 to –60	–75 to –60
<i>T_m</i> (ice) (°C)	–28.8 to –21	–58.8 to –30	–58 to –36
<i>T_m</i> (hyd) (°C)	–7 to 21.9	–	–
<i>T_s</i> (NaCl) (°C)	–	–	115–235
<i>T_h</i> (°C) (mode)	165	115	115
Cl (molal)	5.5–6.5	6	6.5
Na/Ca (mole)	3–7.7	0.5	0.8
Ca/Mg (mole)	1–17.9	1.5	1.7
wt% NaCl	22–24	5	8
wt% CaCl ₂	6–12	20	19
wt% MgCl ₂	0–0.9	11.5	9.5
<i>T_{trapping}</i> (°C)	220 ± 30	110 ± 30	

LIBS, laser-induced breakdown spectroscopy; LA-ICP-MS, laser ablation-inductively coupled plasma-mass spectrometry.

T_e, eutectic melting; *T_m*(ice), ice melting; *T_m*(hyd), hydrohalite melting; *T_s*(NaCl), halite dissolution; *T_h*, total homogenisation. Lw' and Lwh' frequently fail to nucleate any ice upon cooling, and only observed *T_m*(ice) ranges are reported. Inclusions selected for LA-ICP-MS analyses were attributed to the Lw2, Lw' or Lwh' type based on microthermometry.

classified as either NaCl-rich or CaCl₂-rich brine after microthermometry, Lw2 inclusions showing relatively low *T_m*(ice) and Lw'–Lwh' inclusions showing relatively high *T_m*(ice) may represent mixing terms.

Microthermometric data and the corresponding Na–Ca–Mg–K–Sr–Ba–U compositions of selected Lw2, Lw' and Lwh' fluid inclusions are given in Table 2. Sodium is the dominant cation in Lw2 inclusions, while Ca and Mg dominate in Lw' and Lwh' inclusions. Na/Ca and Ca/Mg ratios are fairly consistent with those measured by LIBS on fluid inclusions of similar types by Derome *et al.* (2005) (Table 1). Therefore, according to LIBS and LA-ICP-MS analysis, the Lw2 and Lw'–Lwh' inclusions can be

reliably attributed to the NaCl-rich brine and the CaCl₂-rich brine respectively.

Fluid–rock interaction and brine mixing

Figure 3 shows Ca–Mg–K–Sr–Ba and U concentrations as a function of Na. The interpretations of microthermometric data in terms of NaCl-rich brine or CaCl₂-rich brine composition are highlighted by contrasted symbols. An anticorrelation between Na and Ca–Mg–K–Sr–Ba, as well as a continuum of data between Na-rich and Na-poor compositions, is observed. This trend is interpreted as the result of an incomplete mixing between the NaCl-rich and CaCl₂-rich brines. Possible

compositions of mixing end-members suggest that the NaCl-rich brine has a relatively homogeneous Na–Ca–Mg–K–Sr–Ba concentration, while the CaCl₂-rich brine displays a much greater variability, especially for K, Mg and Sr. About 50% of the analysed inclusions could represent mixing terms.

Low Cl/Br ratios provided by crush–leach analysis in both brines from the McArthur River deposit (Derome *et al.*, 2005) and also from Australian unconformity-related U deposits (Derome *et al.*, 2003, 2007) are compatible with surface evaporation of seawater beyond halite saturation as the dominant mechanism for the acquisition of high salinities. Brine composition can be compared with modern or ancient evaporated seawaters, but with some caution because of uncertainties about c. 1.5 Ga seawater chemistry (Lowenstein and Timofeeff, 2008). Evaporated seawater probably invaded the basis of the Athabasca sandstones, which acted as a huge homogeneous aquifer (Hiatt and Kyser, 2007). Therefore, the significant chemical differences between evaporated seawater and the analysed brines must have been acquired by fluid–rock interaction within the basement rocks, as no evidence for alteration in the basin could account for such compositional changes (McGill *et al.*, 1993). The depletion of K and Mg in the NaCl-rich brine compared with evaporated seawater could be attributed to water–rock interactions producing K and Mg-rich clays such as illite and sudoite. The CaCl₂-rich brine end-member is rich in Mg and K, with concentrations close to those of evaporated seawater, and depleted in Na, thus suggesting a Ca–Na

Table 2 Microthermometric and LA-ICP-MS analyses of selected fluid inclusions.

Fluid type	F.I. type	<i>T_e</i> (°C)	<i>T_m</i> (ice) (°C)	<i>T_m</i> (hyd) (°C)	<i>T_s</i> (NaCl) (°C)	<i>T_h</i> (°C)	Eq. NaCl (wt%)	Na (µg g ^{–1})	Ca (µg g ^{–1})	Mg (µg g ^{–1})	K (µg g ^{–1})	Sr (µg g ^{–1})	Ba (µg g ^{–1})	U (µg g ^{–1})	Na/Ca (mole)	Ca/Mg (mole)
NaCl-rich brine	Lw2	–60	–25.3	4	–	151.5	26.9	87 000	26 000	4300	1700	380	100	n.d.	5.8	3.6
	Lw2	–60	–27.5	6.3	–	127.8	27.2	86 000	32 000	4200	1900	520	130	1.4	4.7	4.6
	Lw2	–60	–25.4	3.9	–	155.9	26.9	79 000	40 000	5600	1800	590	140	n.d.	3.4	4.3
CaCl ₂ -rich brine	Lw2	–60	–27.8	6.8	–	141.7	27.3	75 000	31 000	19 000	4000	550	16	1.0	4.2	1.0
	Lw'	n.f.	n.f.	n.f.	–	77.5	35.0	43 000	76 000	55 000	26 000	2700	45	160	1.0	0.8
	Lw'	n.f.	n.f.	n.f.	–	75	35.0	24 000	83 000	70 000	34 000	3000	<84	n.d.	0.5	0.7
	Lwh'	n.f.	n.f.	n.f.	183	114	28.0	45 000	80 000	24 000	7200	1300	500	<0.5	1.0	2.0
	Lwh'	n.f.	n.f.	n.f.	135	106.5	28.0	38 000	84 000	29 000	11 000	1500	480	<0.5	0.8	1.7

LOD, Limits of detection; LA-ICP-MS, laser ablation-inductively coupled plasma-mass spectrometry.

n.f., no freezing; F.I., fluid inclusion; n.d., not determined because of U contamination. Values preceded by a < symbol stand for element concentrations below the LOD.

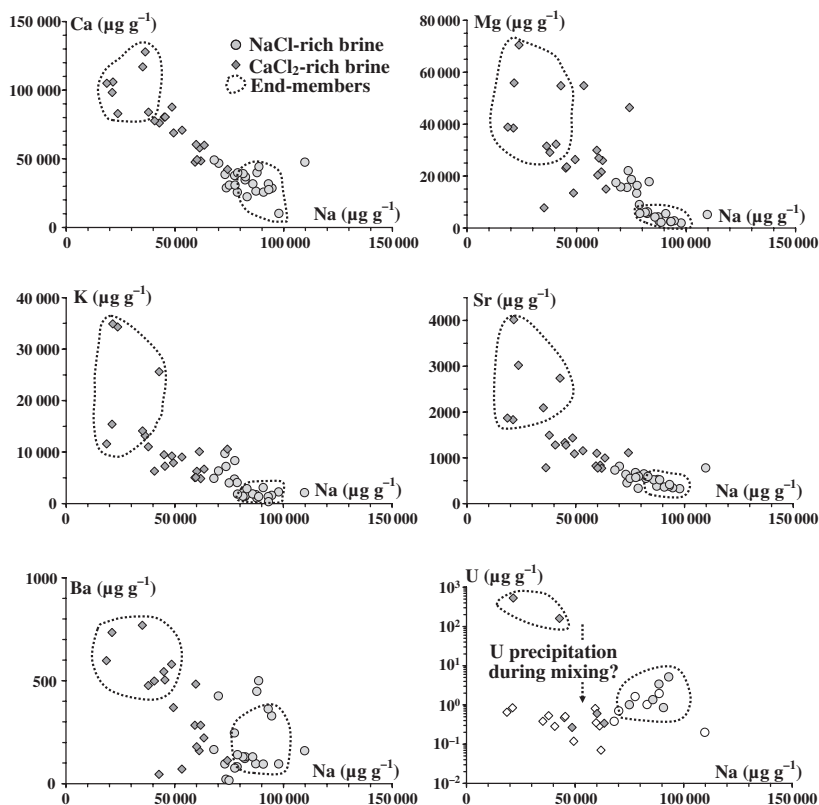


Fig. 3 Na–Ca–Mg–K–Sr–Ba–U relations in analysed fluid inclusions. In the U vs. Na plot, empty symbols stand for limits of detection (LODs) when U was below LOD.

exchange. Compared with the evaporated seawater, it is also significantly enriched in Sr and Ba, correlatively to Ca, which suggests that the Sr and Ba were extracted together with Ca. Albitisation of plagioclase in the basement is the most likely process that is able to liberate sufficient Ca and Sr.

Uranium and trace elements

Although the determination of the U concentration in fluid inclusions in these samples was complicated by local surface contamination (smearing of U during polishing) and the presence of U-rich domains in the host quartz (up to $1 \mu\text{g g}^{-1}$ U), fortunately, 10 inclusions showed reliable U signals with concentrations above LODs ranging from 0.3 – $530 \mu\text{g g}^{-1}$ (Figs 3 and 4). U concentration in the CaCl_2 -rich brine end-member is one to two orders of magnitude higher than that in the NaCl-rich brine end-member. The measured U concentrations are well above those previously reported for common modern basinal

brines (*c.* 10 ng g^{-1} ; Hodge *et al.*, 1996) and document exceptionally high U mineral solubility in these brines. Such concentrations are attributable to the nature of the ore fluids and to redox conditions sufficiently

oxidising to avoid the precipitation of U(IV) minerals (Komninou and Sverjensky, 1995; Kister *et al.*, 2005). U concentrations in the 1 – $1000 \mu\text{g g}^{-1}$ range are expected in high chlorinity solutions from the NaCl–U(VI)– H_2O system at $T = 155^\circ\text{C}$ and $\text{pH} = 4$ – 5 , as shown by recent experimental work (Rozsypal, 2009). Variability in U concentrations among the mixed fluid inclusion types might then document effective precipitation during fluid mixing (Fig. 3).

There are no clear differences between the Li, B, Mn, Fe and Rb contents of the two brines (Fig. 4). Although frequently below LODs, the measured Fe, Mn, Cu, Pb and Zn concentrations are broadly compatible with metal-rich basinal brines and may account for the high capacity of brines to carry metals, and possibly U, as chloride complexes (Fig. 4) (Yardley, 2005).

Genetic implications

The source of U in unconformity-related deposits is still widely debated. Fayek and Kyser (1997) proposed that U was leached from accessory minerals in basinal sandstones. Other authors state that basement alteration is one of the key factors in the genesis of such deposits, as basement rocks contain several potential U sources such as magmatic uraninite (Annesley and Madore, 1999; Madore *et al.*, 2000), pre-Athabasca U mineralisations (Parslow and Thomas, 1982) and

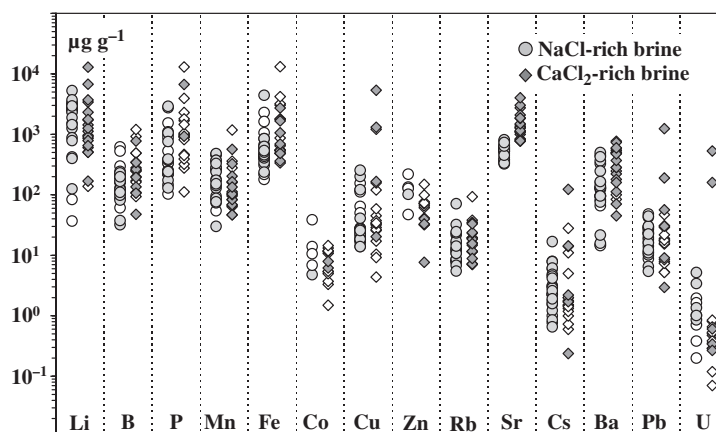


Fig. 4 Range of minor and trace element compositions for the NaCl-rich brine and for the CaCl_2 -rich brine inclusions analysed by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Empty symbols stand for limits of detection (LODs) when elements were below LOD.

monazites (Hecht and Cuney, 2000). Our first fluid data indicate that brine–rock interaction within basement rocks probably controlled the brine composition and could be responsible for its high U content, which would be consistent with a dominant basement U source for the McArthur River deposit. The measured U concentrations are comparable with those used by Raffensperger and Garven (1995) ($20\text{--}30\ \mu\text{g g}^{-1}$) to estimate a duration of 0.1–1 Ma for the formation of such high-grade U deposits.

Redox conditions are unknown but sufficiently oxidising to maintain U(VI) in solution as a complex, probably a uranium chloride. The main mechanism of U reduction is controversial and will not be discussed here. The changes occurring during the mixing of brines (changes in ionic strength and major cation ratios) could be among the major causes of destabilisation of uranyl chloride complexes.

Brine infiltration in the basement was probably favoured by seismic tectonic activity, which produced microfractures and fault opening, as shown by recent coupled microtectonic–microthermometric studies (Mercadier *et al.*, 2010). Therefore, the downward penetration of brines was localised in favourable zones and was not caused by fluid density differences as generally invoked in gravity-driven models. Brine movements and upward migration along faults were probably favoured by both tectonic activity and thermal convection. The main deposit areas were mixing zones for brines coming from two distinct reservoirs, the main sandstone reservoir and the microfractured basement, where both brines evolved chemically and took up the uranium.

Isotopic analyses of alteration minerals have documented mixing between basin-derived and basement-derived fluids (Wilson and Kyser, 1987; Kotzer and Kyser, 1995; Fayek and Kyser, 1997; Alexandre *et al.*, 2009b). Here, we suggest that the NaCl-rich brine and the CaCl₂-rich brine could be the basin-derived and basement-derived fluids respectively. In contrast to the conclusions presented by Alexandre *et al.* (2009b), our results suggest that basement-derived fluids are originally oxidising basinal brines, modified through fluid–

rock interaction causing the gains in U, Ca, Sr and Ba. The basement U reservoir is probably much more significant than the sedimentary basin, as demonstrated for other metals (Koziy *et al.*, 2009; Boiron *et al.*, 2010).

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