

Unconformity-related U deposits: recent advances from fluid inclusions and their host minerals

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Abstract. The Paleoproterozoic Athabasca Basin (Canada) hosts numerous world class unconformity-related uranium deposits. Many aspects of their genesis remain debated. The objective here is to review recent fluid inclusion and stable isotope studies that have contributed to a better understanding of: (1) the origin and P-T-X conditions of the mineralizing fluids; (2) the conditions for transport of metals and in particular uranium; (3) the relationships between fluid chemistry and alteration features (fluid-rock interaction) and (4) some aspects of uranium deposition. As a whole, the Athabasca system was dominated by basinal brines of evaporated-seawater origin. The brines have percolated through reactivated basement structures, leached metals in basement rocks, and caused intensive Mg-B alteration. Furthermore, the brines were anomalously acidic and have transported the uranium at the highest concentration so far reported for crustal fluids. This feature alone could simply explain the spectacular alteration and also the tremendous grades and tonnages of the Athabasca uranium deposits.

Keywords. Unconformity, Uranium, Brines, Fluid Inclusions, Host minerals, Athabasca Basin

1 Geology and fluid inclusion sampling

The Athabasca Basin unconformably overlies an Archean to Paleoproterozoic basement separated into two provinces (the Rae Province in the west and the Hearne Province in the east) by the northeast-trending Snowbird tectonic zone (Fig. 1). These two provinces consist of Archean gneisses, Paleoproterozoic metapelites and mafic to felsic intrusions. They were affected, respectively, by the ~2.0 to ~1.9 Ga Thelon-Talston and the ~1.9 to ~1.8 Ga Trans-Hudson orogenies (Annesley et al. 2005).

The sedimentary sequence of the Athabasca Basin was deposited starting from ~1.75 Ga (Ramaekers et al. 2007). From the base to the top, the Athabasca Group is composed of fluvial to marginal marine quartz-rich sandstones, marine sandstones, phosphatic siltstones, phosphatic mudstones, fluvial sandstones, shales and finally stromatolitic carbonates. The current maximum

thickness of the sedimentary cover is ~1.5 km and could have originally been as much as ~5 km, based on P-T estimations from fluid inclusions (Pagel, 1980; Derome et al. 2005).

The U deposits are generally located near the basement/cover interface, and structurally controlled by sub-vertical faults rooted in graphite-rich basement metapelites. The earliest UO₂ ores in the Athabasca Basin have been dated to between 1.6 and 1.4 Ga and successive late episodes of mineralization, and/or recrystallisation occurred until ~0.7 Ga (Alexandre et al. 2012). Remobilization of primary UO₂ by meteoric fluids likely occurred around 400 Ma and subsequently, until recent times (Mercadier et al., 2011a).

The main alteration features associated with the U-ores include successively: (1) partial to complete replacement of the original basement minerals (K-feldspar, biotite, plagioclase, hornblende) by an illite + sudoite (Mg-chlorite) ± dravite (Mg-tourmaline) assemblage (also referred to as “bleaching”) as well as the precipitation of illite and sudoite in sandstones; (2) quartz dissolution in basement rocks as well as in the sandstones and (3) precipitation of dravite + quartz + UO₂ + dolomite + bitumen in quartz dissolution voids and in veins and breccias (Derome et al., 2005; Mercadier, 2010). Alteration surrounding the U deposits is associated with rare earth element mobilization and redistribution among aluminium phosphate-sulphate minerals and uraninite (Mercadier et al., 2011b).

Sandstone silicification, and quartz and dolomite veins are spatially and temporally associated with the main alteration minerals and U mineralization (Fig. 1). Hence, they are likely to host fluid inclusions that are relicts of the mineralizing fluids. The veins crosscut various lithologies such as basement gneisses and pegmatoids as well as basin sandstones. Veins were sampled in relatively fresh to extensively altered and mineralized rocks.

2 P-T-X characteristics of brines

Two phase (liquid-vapour) or three phase (liquid-vapour-halite) fluid inclusions (5 to 25 μm in size) are typically observed in both quartz and dolomite and secondary fluid inclusion planes in basement quartz (Kotzer and Kyser, 1995; Derome et al. 2005; Mercadier et al. 2010; Richard et al. submitted to Ore Geol Rev). The volumetric proportion of the vapour phase is $\sim 10\%$ (Fig. 1).

Microthermometry and reconstruction of fluid inclusions compositions in the $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$ -system shows that the fluid inclusion salinity is comprised between 25 and 35 wt% equivalent NaCl. Fluid inclusion LA-ICP-MS compositions display a continuum between a NaCl-rich end-member ($\text{Cl} > \text{Na} > \text{Ca} \approx \text{Mg} > \text{K}$) and a CaCl_2 -rich end-member ($\text{Cl} > \text{Ca} \approx \text{Mg} > \text{Na} > \text{K}$). The CaCl_2 -rich brine has the highest salinity and shows evidence for NaCl-saturation at the time of trapping. The majority of homogenization temperature of fluid inclusions is comprised between 100 and 150°C for the NaCl-rich brine, and 80 and 140°C for the CaCl_2 -rich brine end-members (Derome et al. 2005; Richard et al. 2010; Richard et al. submitted to Ore Geol Rev).

The continuum of microthermometric and LA-ICP-MS compositional data between the NaCl-rich brine and the CaCl_2 -rich brine end-members suggest that the two brines have mixed in all deposits at the time of U deposition. P-T reconstructions suggest that mixing was non-isothermal (NaCl-rich brine: $180 \pm 30^\circ\text{C}$ and 800 ± 400 bars; CaCl_2 -rich brine: $120 \pm 30^\circ\text{C}$ and 600 ± 300 bars) and occurred under fluctuating pressure conditions (hydrostatic to supra-hydrostatic).

3 Brine flow in crystalline basement

Detailed analysis of oriented secondary fluid inclusion planes within magmatic and metamorphic quartz in basement rocks reveals that the NaCl-rich and CaCl_2 -rich brines have penetrated extensively into the basement not only through faults and major pathways (as shown by quartz and dolomite veins) but also by way of dense networks of microfractures which favoured the percolation of fluids at least hundred metres below the unconformity (Mercadier et al. 2010).

Microfracture networks, which opened during the basinal brine stage (ca. 1600–1400 Ma) are interpreted as sets of mode I cracks corresponding to a specific stage of deformation and occur as fluid inclusion planes after healing. The stress field at that stage ($\sigma_1 = \text{N}130\text{--}150^\circ\text{E}$, subvertical) partly reopened the earlier microcrack networks ($\sigma_1 = \text{N}80\text{--}110^\circ\text{E}$ and $\text{N}130\text{--}150^\circ\text{E}$, subvertical) inherited from late retrograde metamorphic stage of the Trans-Hudson Orogeny (ca. 1795–1720 Ma).

This demonstrates the existence of a similar stress field direction acting before and after the basin formation. Moreover, the brine circulations in the basement acted throughout a wider volume than the clay-rich alteration halo surrounding the U-ores, generally considered as the main envelope of fluid percolation outside the fault systems. The data on the chemistry of the fluids and on the geometry of their migration at various scales emphasise the fundamental role of the

basement in the chemical evolution of highly saline brines, as for many other Proterozoic to recent U and base metal basin-hosted systems (Boiron et al. 2010)

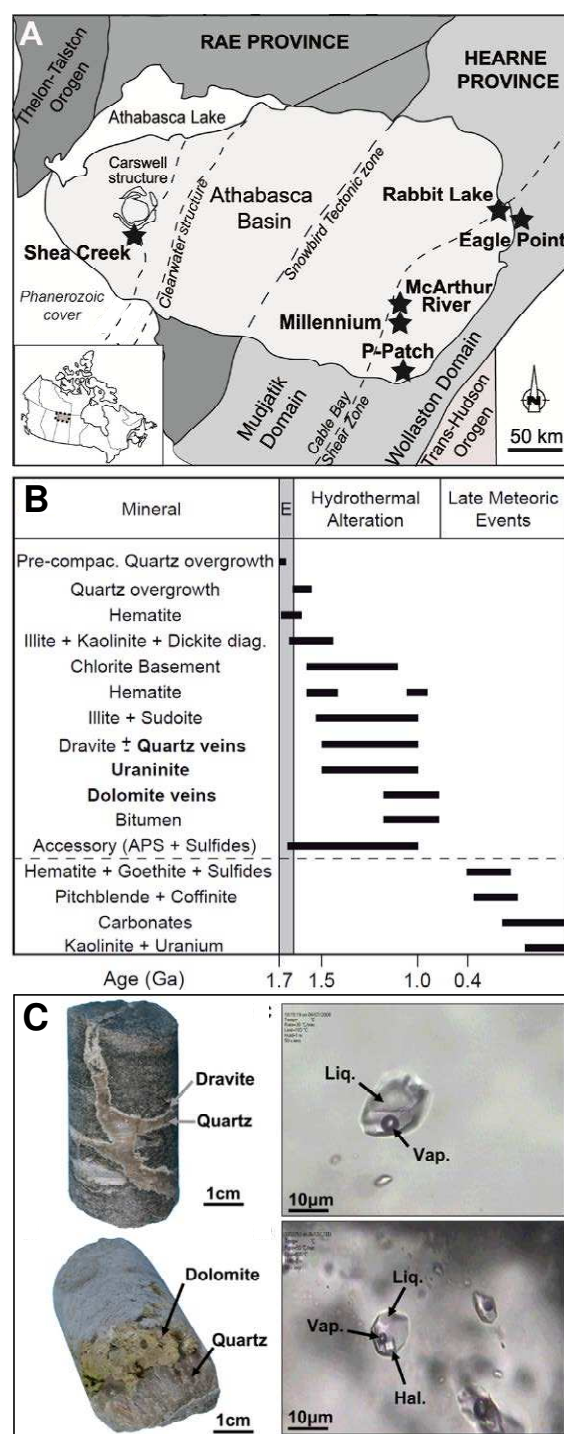


Figure 1. (A) Simplified geological map of the Athabasca Basin and Basement, Canada. Stars indicate the studied deposits. (B) Simplified mineral successions (E: early diagenetic, hydrothermal and late meteoric) for unconformity-related U deposits in the Athabasca Basin (modified from Mercadier et al. (2012) and references therein). APS: aluminium phosphate-sulphate (C) Example of quartz and carbonate veins, hosting fluid inclusions studied in this work (Richard et al. 2011).

4 Origin of brines

Noble gas, crush-leach, stable chlorine isotope and LA-ICP-MS analyses of fluid inclusions show that the brines have molar Br/Cl ratios from 5×10^{-3} to 10×10^{-3} , and I/Cl ratios from 2×10^{-6} to 12×10^{-6} , and $\delta^{37}\text{Cl}$ values of -0.6 and 0‰ (Richard et al. 2011; Leisen et al. 2012; Richard et al. submitted to Precambrian Res). These compositions are consistent with the fluids deriving the bulk of their salinity by sub-aerial evaporation of seawater, beyond the point of halite saturation.

The chloride has an unambiguous, dominantly marine origin and has required large-scale seawater evaporation and minor evaporite deposition. Although direct evidence for evaporative environments in the Athabasca Basin is lacking due to the erosion of ~80% of the sedimentary pile, halogens have behaved conservatively at the basin scale and throughout basin history.

Stable boron isotope compositions of dravite (Mg-tourmaline) ($\delta^{11}\text{B} = 19.6\text{‰}$ to 36.5‰) associated with quartz and dolomite veins indicate that most of the boron has a marine origin, consistent with halogen data. Because evaporated-seawater is typically Mg-rich, it is proposed that the Mg enrichment in altered rocks (Mg-tourmaline, Mg-chlorite) is due to the input of Mg-rich evaporated-seawater brines (Mercadier et al. 2012).

5 Fluid-rock interaction

$\delta^{18}\text{O}$ values of quartz veins ($\delta^{18}\text{O} = 11\text{‰}$ to 18‰) and previously published $\delta^{18}\text{O}$ values of the dominant alteration minerals (illite, chlorite and tourmaline), show that quartz and alteration minerals were isotopically equilibrated with the same fluid at ~180°C (Richard et al. 2013a).

The $\delta^{13}\text{C}$ values of trace amounts of CO_2 dissolved in dolomite-hosted fluid inclusions ($\delta^{13}\text{C} = -30.1\text{‰}$ to -3.8‰) and the $\delta^{13}\text{C}$ values of dolomite ($\delta^{13}\text{C} = -23.5\text{‰}$ to -3.5‰) indicate that CO_2 originates from brine-graphite interaction in the basement. The calculated $\delta^{18}\text{O}$ values of the mineralizing brines ($\delta^{18}\text{O} = -1\text{‰}$ to 8‰) have shifted considerably from those acquired during evaporation of seawater, as has the δD value as measured directly on fluid inclusions ($\delta\text{D} = -150\text{‰}$ to -50‰). The positive $\delta^{18}\text{O}$ shift is explained by protracted fluid-rock interaction within the basin and basement rocks. The negative δD shift is attributed to incomplete mixing between the brines and low δD water. This low δD water is likely to have been produced during the abiogenic synthesis of bitumen by Fisher-Tropsch-like reactions involving CO_2 derived from brine-graphite interaction, and radiolytic H_2 . (Richard et al. 2013a).

Several scenarios are proposed to account for the chemical conversion of evaporated seawater into a NaCl-rich and a CaCl_2 -rich brine. It appears that a combination of dolomitization, mixing with halite-dissolution brine and albitization accounts for the observed composition of the NaCl-rich brine. The CaCl_2 -rich brine possibly acquired its Ca-dominated composition by extensive albitization although petrographic evidence to support this is lacking. This suggests that the two brines have had distinct flow

paths and fluid-rock interaction histories in the Athabasca Basin and Basement (Richard et al. 2013a; Richard et al. submitted to Ore Geol Rev).

The majority of samples contain fluid inclusions with age-corrected $^{40}\text{Ar}/^{36}\text{Ar}$ of between the modern atmospheric value of ~300 and 450. These values are typical of upper crustal sedimentary formation waters. $^{40}\text{Ar}_\text{E}$ concentrations are between 0.03 and $0.8 \mu\text{g.g}^{-1}$ ($^{40}\text{Ar}_\text{E}$ denotes crustally-derived excess ^{40}Ar). Fluid inclusion non-radiogenic $^{84}\text{Kr}/^{36}\text{Ar}$ and $^{129}\text{Xe}/^{36}\text{Ar}$ ratios are intermediate to between air and air-saturated brines. The fluids contain 1.9 to 62 ppb ^{36}Ar which is up to twenty times the ^{36}Ar concentration of air-saturated seawater. The noble gas data are interpreted to reflect acquisition of atmospheric ^{36}Ar , ^{84}Kr and ^{129}Xe from sedimentary rocks. The lack of a strong enrichment in radiogenic ^{40}Ar and preservation of low $^{40}\text{Ar}/^{36}\text{Ar}$ ratios suggests that interaction of the brines with basement rocks occurred at high water-rock ratios or low temperatures (<200°C) (Richard et al. Submitted to Precambrian Res).

6 U and metal transport

LA-ICP-MS analysis of fluid inclusions shows that the two brines have high content: up to $600 \mu\text{g.g}^{-1}$ U, $3000 \mu\text{g.g}^{-1}$ Mn, $4000 \mu\text{g.g}^{-1}$ Zn, $6000 \mu\text{g.g}^{-1}$ Cu and $8000 \mu\text{g.g}^{-1}$ Pb. The CaCl_2 -rich brine carries ~ one order of magnitude more metals than the NaCl-rich brine (Richard et al. 2010; 2012; Richard et al. submitted to Ore Geol Rev).

Fluid inclusions from two quartz samples of the McArthur River and Rabbit Lake deposits were analysed by synchrotron X-ray fluorescence (SXRF) and X-ray absorption near-edge spectroscopy (XANES). SXRF results show that fluid inclusions contain appreciable amounts of Br, Fe, Sr, transition metals (Mn, Ni, Cu, Zn), Pb, U and rare earth elements (REE) (La, Ce). XANES on 4 McArthur River sample fluid inclusions at room temperature and at 150°C (homogenized fluid inclusion) as well as in solid and liquid U(IV) and U(VI) standards, respectively, shows that the uranium has remained in the form of U(VI) from the time of trapping to the present in the fluid inclusion (Richard et al. 2013b).

The metal (Cu, Pb, Zn, Mn, Fe) concentrations are comparable to the highest recorded in present-day sedimentary formation waters and in fluid inclusions from basin-hosted base metal ore deposits for which a basement metal source has been frequently proposed. Trends between Cu, Pb, Zn, Mn, Fe and U concentrations in fluid inclusions suggest that the metals were leached from a proximal source, basement rocks being the most likely candidate (Richard et al. 2012; Richard et al. submitted to Ore Geol Rev).

The solubility of U(VI) was measured experimentally as a function of NaCl content and pH in mixtures that are analogous to ore-forming brines at 155°C. To account for the high uranium content observed in the fluid inclusions, the brines must have been unexpectedly acidic, with a pH between 2.5 and 4.5. Although the origin of acidity in the studied brines remains to be better

understood, it seems that pH is a key factor contributing to the highly efficient transport of uranium in the Athabasca system (Richard et al. 2012).

7 UO₂ deposition

UO₂ deposition requires reduction of U(VI) to U(IV) and is one of the least understood processes in these deposits. Fluid inclusion data do not allow us to determine precipitation mechanism here but put at least some constraints on plausible vs implausible hypotheses. Raman spectrometry shows that trace amounts of potentially reducing gases (e.g. CH₄, H₂) are present (Derome et al 2003a). Mg-rich alteration has long been regarded as originating from a basement-derived reducing fluid, but from the present studies is now considered as originating from evaporated seawater-derived brines (Mercadier et al. 2012). The low I/Cl ratios do not favour fluid interaction with organic matter, or hydrocarbons, as a reductant (Richard et al. Submitted to Precambrian Res).

8 Conclusion and perspectives

Detailed characterization of fluid inclusions in the Athabasca basin has allowed us to better understand many genetic aspects of their genesis. Mechanisms for quartz dissolution and UO₂ deposition remain enigmatic. More comparative work on Australian unconformity-related U deposits (Derome et al. 2003b; 2007) and other Proterozoic to recent U and base metal basin-hosted systems (Boiron et al. 2010) would be helpful to better understand large-scale brine circulation at basement-cover interfaces and metal transport.

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