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From evaporated seawater to uranium-mineralizing brines: Isotopic and trace element study of quartz–dolomite veins in the Athabasca system

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Abstract

Stable isotope (O, H, C), radiogenic isotope (Sr, Nd) and trace element analyses have been applied to quartz–dolomite veins and their uranium(U)-bearing fluid inclusions associated with Proterozoic unconformity-related UO_2 (uraninite) ores in the Athabasca Basin (Canada) in order to trace the evolution of pristine evaporated seawater towards U-mineralizing brines during their migration through sediments and basement rocks.

Fluid inclusion data show that quartz and dolomite have precipitated from brines of comparable chemistry (excepted for relatively small amounts of CO_2 found in dolomite-hosted fluid inclusions). However, $\delta^{18}\text{O}$ values of quartz veins ($\delta^{18}\text{O} = 11\text{‰}$ to 18‰) and dolomite veins ($\delta^{18}\text{O} = 13\text{‰}$ to 24‰) clearly indicate isotopic disequilibrium between quartz and dolomite. Hence, it is inferred that this isotopic disequilibrium primarily reflects a decrease in temperature between the quartz stage ($\sim 180^\circ\text{C}$) and the dolomite stage ($\sim 120^\circ\text{C}$). The $\delta^{13}\text{C}$ values of CO_2 dissolved in dolomite-hosted fluid inclusions ($\delta^{13}\text{C} = -30\text{‰}$ to -4‰) and the $\delta^{13}\text{C}$ values of dolomite ($\delta^{13}\text{C} = -23.5\text{‰}$ to -3.5‰) indicate that the CO_2 dissolved in the mineralizing brines originated from brine–graphite interactions in the basement. The resulting slight increase in the fluid partial pressure of CO_2 ($p\text{CO}_2$) may have triggered dolomite precipitation instead of quartz.

$\delta^{18}\text{O}$ values of quartz veins and previously published $\delta^{18}\text{O}$ values of the main alteration minerals around the U-ores (illite, chlorite and tourmaline) show that quartz and alteration minerals were isotopically equilibrated with the same fluid at $\sim 180^\circ\text{C}$. The REE concentrations in dolomite produce PAAS-normalized patterns that show some similarities with that of UO_2 and are clearly distinct from that of the other main REE-bearing minerals in these environments (monazite, zircon and aluminum phosphate–sulfate (APS) minerals). The radiogenic isotope compositions of dolomite ($^{87}\text{Sr}/^{86}\text{Sr}_i = 0.7053$ to 0.7161 and $\varepsilon_{\text{Nd}}(t) = -8.8$ to -20.3) differ from one deposit to another, reflecting both heterogeneity in the basement geology and variable preservation of the original composition of brines. The previously published $^{87}\text{Sr}/^{86}\text{Sr}_i$ and $\varepsilon_{\text{Nd}}(t)$ values of UO_2 compare with the most evolved dolomites, i.e. dolomites precipitated from brines that exchanged the most with the basement. This reinforces a close genetic link between dolomites and UO_2 deposition and implies that UO_2 deposition occurred in a cooling system during the transition from quartz to dolomite formation.

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The $\delta^{18}\text{O}$ and δD values of the mineralizing brines ($\delta^{18}\text{O} = -1\text{‰}$ to 8‰ and $\delta\text{D} = -150\text{‰}$ to -50‰) are considerably shifted from that of their theoretical original values acquired during evaporation of seawater ($\delta^{18}\text{O} = \sim -3\text{‰}$ and $\delta\text{D} = \sim -40\text{‰}$). 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 U-mineralizing brines and low δD water. This low δD water was likely produced during the abiogenic synthesis of bitumen by Fisher–Tropsch-like reactions involving CO_2 derived from brine–graphite interaction in the basement, and radiolytic H_2 . The resulting low δD brines have been equilibrated with alteration minerals. This may explain why some alteration minerals yield anomalously low δD values whose significance has long been debated.

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1. INTRODUCTION

A variety of mineral deposits are thought to have formed from brines derived from seawater evaporation (e.g. [Kesler et al., 1995](#); [Essarraj et al., 2005](#); [Muechez et al., 2005](#); [Richard et al., 2011](#)). Due to their high ionic strength, pristine evaporated seawaters are highly reactive fluids which may scavenge metals in the rocks through which they circulate and ultimately form mineral deposits. Hence, tracing brine–rock interaction in such brine-related systems could greatly help deciphering some key aspects of the ore-forming processes.

The Proterozoic Athabasca Basin (Saskatchewan, Canada) hosts numerous ‘unconformity-related’ uranium (U) deposits located close to the interface between the Archean to Paleoproterozoic crystalline basement, the late-Paleoproterozoic sedimentary cover and reactivated basement-rooted faults ([Jefferson et al., 2007](#); [Kyser and Cuney, 2008](#)). The ~ 1.5 to ~ 1.0 Ga UO_2 (uraninite) ores document protracted and large-scale circulation of basin-derived oxidizing U-rich brines at the basement/cover interface (e.g. [Hoeve and Sibbald, 1978](#); [Kotzer and Kyser, 1995](#); [Fayek and Kyser, 1997](#); [Kyser et al., 2000](#); [Derome et al., 2005](#); [Boiron et al., 2010](#); [Richard et al., 2012](#)).

The origin of the basinal brines has been investigated based on coupled Cl/Br and $\delta^{37}\text{Cl}$ composition of fluid inclusions and $\delta^{11}\text{B}$ composition of Mg-tourmaline (dravite) associated to U ores ([Richard et al., 2011](#); [Mercadier et al., 2012](#)). These studies have shown that the mineralizing brines originate from evaporation of seawater beyond halite saturation, and reached a salt content of ~ 30 wt.% before percolating through the sedimentary pile and the crystalline basement. Since the primary origin of brines is known, stable isotope (O, H, C), radiogenic isotope (Sr, Nd) and trace element analyses can be applied to quartz–dolomite veins and their fluid inclusions associated with U-ores, in order to highlight the processes occurring during the evolution of evaporated-seawater towards U-mineralizing brines. While few data exist in the literature regarding the stable isotope composition (O, H, C) of quartz and dolomite veins and their fluid inclusions associated with the Athabasca Basin ore bodies ([Pagel et al., 1980](#); [Hoeve et al., 1986](#); [Wilson and Kyser, 1987](#); [Kotzer and Kyser, 1995](#)), no Sr and Nd isotopic and trace element data have been reported for dolomite veins.

Along the brine flow path, brine–rock interactions have been key events in the mineralizing process because: (i) brine–rock interactions are at the origin of the chemical

evolution of evaporated seawater into two chemically distinct NaCl-rich and CaCl_2 -rich brines, whose mixing is coeval with UO_2 deposition ([Derome et al., 2005](#); [Richard et al., 2010](#)); (ii) basin and basement rocks contain various potential U sources ([Fayek and Kyser, 1997](#); [Hecht and Cuney, 2000](#); [Mercadier et al., in press](#)) and (iii) basement rocks host potential U-reducing agents, necessary for the reduction of U(VI) to U(IV) and UO_2 deposition ([Hoeve and Quirt, 1987](#)).

Many aspects of the evolution of brines through brine–rock interaction and U mineralization remain contentious and are addressed in this paper: (i) the degree of isotopic (and chemical) equilibration between the brines and host rocks ([Pagel et al., 1980](#); [Wilson and Kyser, 1987](#); [Kotzer and Kyser, 1995](#)); (ii) the magnitude of temperature variation during the ore-forming events (e.g. [Alexandre et al., 2005](#); [Derome et al., 2005](#)); (iii) the mobility of REE which can substitute for up to ~ 1 wt.% of the U in UO_2 ([Fayek and Kyser, 1997](#); [Mercadier et al., 2011a](#)) and whose content is in the order of tens to hundreds of ppm La and Ce in the fluid inclusions ([Richard et al., in press](#)); (iv) the nature of gases produced by interaction between brines and graphitic metapelites in the basement (e.g. [Bray et al., 1988](#); [Kyser et al., 1989](#)) and (v) the origin of anomalously-low δD values of alteration minerals around U-ores (e.g. [Halter et al., 1987](#); [Kotzer and Kyser, 1991](#)).

2. GEOLOGY, SAMPLING AND FLUID INCLUSIONS

2.1. Regional geology

The Athabasca Basin unconformably overlies the Archean to Paleoproterozoic Western Churchill Province separated into two Subprovinces (the Rae Subprovince in the west and the Hearne Subprovince in the east) by the North-east-trending Snowbird tectonic zone ([Hoffman, 1990](#); [Card et al., 2007](#); [Jefferson et al., 2007](#)) (Fig. 1A). These two subprovinces 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 ([Chiarrenzelli et al., 1998](#); [Annesley et al., 2005](#)). A majority of the known unconformity-related U deposits of the Athabasca Basin, are located close the transition between two lithostructural domains of the Hearne Subprovince, known as the Wollaston–Mudjatik transition zone that consists of a Northeast-trending, anastomosing structure of Hudsonian age (1.8 Ga) ([Annesley et al., 2005](#)).

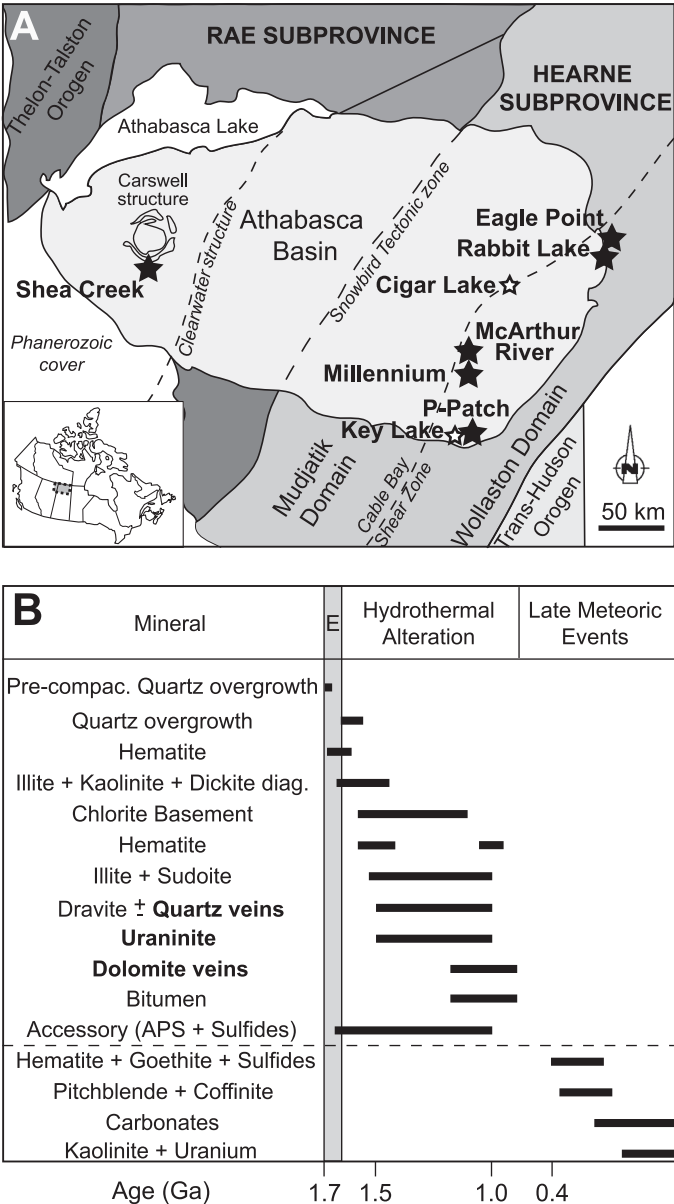


Fig. 1. (A) Simplified geological map of the Athabasca Basin and its underlying Rae and Hearne Subprovinces, with location of the six studied unconformity-related U deposits (full stars) (modified from Card et al. (2007) and Jefferson et al. (2007)). Cigar Lake and Key Lake deposits (empty star) were not studied here but are mentioned in the text. (B) Simplified mineral paragenesis for unconformity-related U deposits in the Athabasca Basin. The type of alteration (E: early diagenetic, hydrothermal and late meteoric), their temperature and timing are indicated. Diag.: diagenetic. Modified from Kotzer and Kyser (1995), Derome et al. (2005), Kyser and Cuney (2008) and Mercadier et al. (2011b).

The sedimentary sequence of the Athabasca Basin (the Athabasca Group), was deposited starting from ~1.75 Ga (Ramaekers et al., 2007). The current maximum thickness of the sedimentary cover is ~1.5 km and could have reached ~5 km based on *P–T* estimations from fluid inclusions (Pagel, 1975; Derome et al., 2005). From the base to the top, the Athabasca Group is composed of fluvial to marginal marine quartz-rich sandstones (Fair Point, Read, Smart and Manitou Falls Formations), marine sandstones, phosphatic silt-

stones, and phosphatic mudstones (Lazenby Lake and Wolverine Point Formations), fluvial sandstones (Locker Lake and Otherside Formations), shales (Douglas Formation) and finally stromatolitic carbonates (Carswell Formation) (Ramaekers et al., 2007). The Douglas and Carswell formations are only preserved around the Carswell meteoritic structure (Pagel et al., 1985; Genest et al., 2010).

2.2. Unconformity-related U deposits

The unconformity-related U deposits are generally located near the basement/cover interface, and structurally controlled by sub-vertical faults rooted in graphite-rich basement metapelites. The spatial distribution of the ore and alteration minerals around the unconformity greatly vary between the deposits. The UO_2 ores can be basement-hosted (e.g. P-Patch, Eagle Point and Millennium), unconformity-hosted (e.g. McArthur River, Rabbit Lake) or sandstone-hosted (e.g. Cigar Lake) sometimes in the same deposit (e.g. Shea Creek).

The earliest UO_2 ores in the Athabasca Basin have been dated between 1.5 and 1.4 Ga and successive late episodes of mineralization and/or recrystallization occurred up to ~ 0.7 Ga (Cumming and Krstic, 1992; Fayek et al., 2002; Alexandre et al., 2009a, 2012). Remobilization of primary UO_2 by meteoric fluids likely occurred around 400 Ma and then up to recent times (Mercadier et al., 2011b).

The main alteration features associated with U ores include successively: (i) partial to complete replacement of the initial basement minerals (K-feldspar, biotite, plagioclase) by an illite + sudoite (Mg-chlorite) $\pm$ dravite (Mg-tourmaline) assemblage (also referred as “bleaching”) as well as the precipitation of illite and sudoite in sandstones; (ii) quartz dissolution in basement rocks as well as in the sandstones; (iii) precipitation of dravite + quartz + UO_2 + dolomite + bitumen in quartz dissolution vugs and in veins and breccias (Derome et al., 2005; Mercadier, 2010). A simplified mineral paragenesis summarizing petrographical observations of U deposits throughout the Athabasca Basin is shown in Fig. 1B. Quartz and dolomite veins are spatially associated with the main alteration minerals and U mineralization (Fig. 1B; Pagel et al., 1980; Kotzer and Kyser, 1995; Kyser et al., 2000; Derome et al., 2005).

2.3. Sampling and samples

Six U deposits from the Athabasca Basin have been sampled for this study (McArthur River, Rabbit Lake, Shea Creek, P-Patch, Millennium and Eagle Point), covering various mineralized areas in the basin (Fig. 1A). These deposits share the typical characteristics of unconformity-related U deposits described above (Hoeve and Sibbald, 1978; Heine, 1986; Kotzer and Kyser, 1995; Lorilleux et al., 2002; Derome et al., 2005; Alexandre et al., 2005; Laverret et al., 2006, 2010; Le Carlier de Veslud et al., 2009; Cloutier et al., 2009, 2011; Mercadier et al., 2010, 2011b).

Sampling was mainly focused on basement-hosted vein systems, consistently with the aim to track brine–rock interaction, and also because of a lack of preserved sedimentary cover (i.e. Rabbit Lake and Eagle Point) and lack of sandstone-hosted veins (P-Patch and Millennium). Only four quartz veins were sampled in sandstones at Shea Creek (IF23, IF29, IF41, IF98) at 20–30 m above the unconformity. A total of 49 quartz veins and 20 dolomite veins were sampled, the depth of which below the unconformity ranged from 13 m (EPE44-17, Eagle Point) to 361 m (EPE44-

14, Eagle Point; Table 1). The veins crosscut various lithologies such as gneisses, pegmatoids and sandstones, with varying degrees of alteration. Fig. 2A–F shows some typical quartz and dolomite veins studied in this work. In veins containing both quartz and dolomite (Fig. 2C and D), dolomite growth post-dates quartz growth.

2.4. Fluid inclusions

In quartz and dolomite veins, mainly 5–25 μm two phase (liquid + vapor) and three phase (liquid + vapor + halite) fluid inclusions are observed (Fig. 2G; Pagel et al., 1980; Derome et al., 2005). The volumetric fraction of the vapor phase is between 5% and 15% with maximum frequency around 10%. A minority of inclusions contain solids such as hematite and/or phyllosilicates, both interpreted as daughter minerals due to their relatively constant volume compared to the volume of fluid inclusions. The fluid inclusions have negative crystal or more irregular shapes and are found either along growth bands of the host mineral, as clusters of fluid inclusions, or as isolated inclusions. Therefore, the petrographic evidence suggests that the brine inclusions are either primary or pseudosecondary and coeval with the formation of their host minerals. Very minor amounts of low-salinity inclusions similar to those described in Derome et al. (2005) are present along secondary fluid inclusion planes indicative of healed microfractures.

Detailed microthermometric analysis and P – T reconstruction of quartz-hosted fluid inclusions from McArthur River revealed that the brines at the time of origin of quartz veins formation circulated at temperatures of ~ 110 – 220 $^{\circ}\text{C}$ (Derome et al., 2005). Analyses of fluid inclusions hosted in quartz veins associated with the U ores (microthermometry, laser-induced breakdown spectroscopy (LIBS) and laser ablation-inductively coupled-mass spectrometry (LA-ICP-MS)) have enabled reconstruction of the chemical composition of the U-mineralizing brines. A continuum of compositions between a Cl–Na–Ca–Mg–K brine end-member (“NaCl-rich brine”) and a Cl–Ca–Mg–Na–K end-member (“ CaCl_2 -rich brine”) has been interpreted as the result of mixing between the two end-members at the time of U deposition (Derome et al., 2005; Richard et al., 2010). The two brines have a salinity of 25–35 wt.% salts and have carried U in concentrations up to ~ 600 ppm (Richard et al., 2010, 2012). Synchrotron analyses of U-bearing fluid inclusions have shown that the U remains in the U(VI) form (the most soluble form) at room temperature and up to homogenization temperature (150–200 $^{\circ}\text{C}$) (Richard et al., in press).

Here, the fluid inclusions in the studied samples (quartz and dolomite veins) share all the petrographic characteristics typical of those found in the Athabasca deposits. Detailed microthermometric data for the studied samples will be presented in a separate publication (Richard et al., submitted for publication). Briefly, microthermometric observations have shown that the samples analyzed here contain variable amounts of the NaCl-rich brine and CaCl_2 -rich brine. Homogenization temperatures in quartz- and dolomite-hosted fluid inclusions are predominantly 80 and 150 $^{\circ}\text{C}$, and comparable to those found at McArthur

Table 1

O, H (vs. V-SMOW), C (vs. V-PDB) composition of quartz and dolomite veins and their fluid inclusions from Athabasca Basin and Basement, with location and petrographic description. U/C: unconformity (negative depths indicate that samples were taken in the sandstones). When the depth is unknown, sst and bst indicate that the samples were taken in the sandstones or in the basement respectively. Mineral and rock abbreviations: Qtz: quartz; Dol; dolomite; Hem: hematite; Drv: dravite; Ill: Illite; Chl: chlorite; Pegm: pegmatoid. “Bleached” stands for samples altered to illite–chlorite–dravite assemblages.

Sample	Depth below U/C (m)	Description	Quartz veins		Dolomite veins			
			Fluid inclusions	Quartz	Fluid inclusions		Dolomite	
			δD (H ₂ O)	δ ¹⁸ O	δD (H ₂ O)	δ ¹³ C (CO ₂)	δ ¹⁸ O	δ ¹³ C
<i>Eagle point</i>								
EPE44-17	13	Qtz vein in fresh porphyry granite		16.2				
ES287-1	40	Dol vein in fresh pelitic gneiss			−55	−15	23.3	−4.5
DDH2306-1	130	Qtz-sulfides vein in illitized pegm	−67	16.0				
DDH2306-2	135	Qtz vein in illitized gneiss		16.8				
H1935-2	153	Dol vein in chloritized pegm					13.4	−5.3
H1935-4	159	Hem-dol vein in hem-chl-rich pegm					21.1	−5.3
H1935-5	159	Qtz vein in hematized chloritized gneiss		16.4				
H1935-8	177	Dol-hem vein in biotite-rich gneiss			−62	−19	15.1	−5.4
DDH1733-14	179	Qtz vein in bleached pegm		16.3				
EPE44-4	211	Qtz vein in microgranite		16.0				
287-14	248	Qtz-dol vein in chloritized gneiss		15.3				
287-8	253	Qtz vein in bleached pelitic gneiss		16.1				
287-10	259	Qtz vein in bleached pelitic gneiss	−89	16.3				
EPE44-11	263	Hem-dol vein in chloritized pegm					17.3	−11.2
H3042-1	263	Qtz-drv vein in graphite-rich gneiss	−72	16.3				
ES287-13	272	Qtz cement in clay-hem-rich breccia		16.8				
EPE44-14	361	Dol vein in chloritized pegm					20.5	−7.4
ES287-23	429	Qtz vein in hematized chloritized pegm	−91	16.5				
<i>McArthur River</i>								
MAC48Qz	−42	Qtz vein surrounding U ore		11.9				
MAC8Qz	sst	Qtz-sulfides vein in silicified sst	−68	16.0				
MAC13Qz	sst	Qtz-drv breccia in silicified sst	−102	12.6				
MAC5	25	Qtz-dol vein surrounding U ore	−58	14.2	−147	−30	19.7	−23.5
MAC54Qz	50	Qtz-drv-sulfides in chl-rich breccia	−108	14.6				
<i>Millennium</i>								
CX52-1	99	Qtz-dol vein in bleached gneiss	−107	16.6				
CX48-03	130	Qtz-drv vein in bleached gneiss	−101	15.6				
CX44-2	213	Qtz vein in fresh gneiss	−83	15.9				
CX48-01-12a	265	Qtz vein in hematized gneiss		17.4				
CX51	bst	Qtz filling vugs in hem-ill-chl breccia		16.3				
<i>P-Patch</i>								
P55-15	24	Dol vein in chloritized gneiss					23.5	−9.4
P48-1	29	Qtz vein in chloritized gneiss	−79	16.5				
P48-2	39	Qtz vein in chloritized gneiss	−79	16.6				
P48-3	40	Qtz-dol vein in chloritized gneiss	−77	15.9	−97	−19	19.4	−5.6

P53-10	42	Dol vein in fresh pelitic gneiss					15.6	−6.5
P48-5	52	Qtz vein in bleached gneiss	−66	16.1				
P54-5	64	Qtz vein in fresh gneiss	−92	16.3				
P53-6	96	Qtz vein in ill-chl-rich pegm	−110	15.6				
P63-6	104	Massive dolomite with chl patches			−81	−9	19.2	−4.0
P57-2	104	Qtz vein in bleached pegm	−104	14.8				
P70-1	122	Qtz-dol-hem-driv breccia	−89	15.8				
P49-4	149	Dol vein in chloritized gneiss					22.8	−5.1
P56-17	164	Qtz-driv veins in ill-rich pelitic gneiss	−91	13.9				
<i>Rabbit lake</i>								
DDH197-2	21	Qtz vein in gneiss	−82	16.4				
DDH7-1	125	Qtz filling vugs in dequartzified gneiss		15.9				
DDH7-32-8	300	Qtz filling vugs in dequartzified gneiss		15.0				
DDH197-5	bst	Dol-chl vein in gneiss			−66	−16	14.5	−5.3
RB3Qz1	bst	Qtz cementing chl-driv breccia		15.5				
RBL11Carb	bst	Dol in bleached gneiss			−62	−8	16.1	−5.1
RBL14	bst	Qtz-dol vein in gneiss	−79	13.4	−46	−4	20.5	−4.5
RBL1	bst	Qtz-dol vein in gneiss		13.6	−48	−11	16.6	−4.9
RBL2	bst	Qtz-dol vein in hem-rich gneiss	−80	13.0	−64	−12	14.4	−4.8
RBL3Qz	bst	Qtz fragment in chl-driv breccia	−92	14.7				
RBL4Qz	bst	Qtz-dol vein in gneiss		16.5				
RBL5	bst	Qtz-dol vein in hydraulic megabreccia	−98	15.2	−53	−12	13.1	−6.6
RBL7	bst	Qtz-dol vein in hydraulic megabreccia	−103	15.5	−60	−16	15.9	−5.0
RBL9	bst	Qtz-dol vein in gneiss	−83	16.2			13.7	−6.3
<i>Shea creek</i>								
SHE03 externe	sst	Qtz vein in bleached sst		16.7				
IF74	sst	Qtz-driv breccia in sandstones		14.1				
SHE123-9-H503	50	Qtz-driv veins in chloritized gneiss		12.9				
SHE123-9-H506	62	Qtz-hem vein in bleached gneiss	−94	15.8				
SHE38a	63	Qtz vein in gneiss		15.4				
ERC5-922.0	195	Qtz-hem vein in hematized gneiss	−52	16.9				

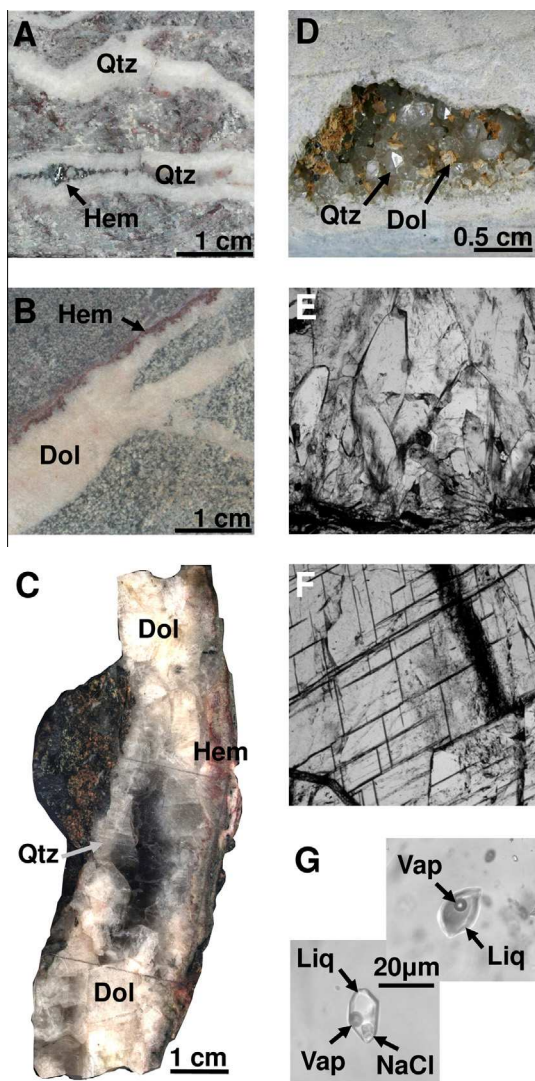


Fig. 2. Examples of quartz and dolomite veins and their fluid inclusions studied in this work. (A) Quartz and quartz-hematite veins crosscutting a hematite-rich gneiss (sample ERC5-922.0, Shea Creek). (B) Hematite-dolomite vein crosscutting a biotite-rich gneiss (sample H1935-8, Eagle Point). (C) Quartz-dolomite vein crosscutting a hematite-rich gneiss (sample RBL2, Rabbit Lake). (D) Quartz-dolomite vein crosscutting "bleached" (illite-chlorite-dravite alteration) gneiss (sample CX52-1, Millennium). (E) Close up on one quartz vein showing multiple individual quartz crystals (view on thick section, sample RBL2, Rabbit Lake). (F) Close up on one dolomite vein showing multiple individual dolomite crystals (view on thick section, sample RBL2, Rabbit Lake). (G) Primary two-phase (liquid + vapor) and three-phase (liquid + vapor + halite) fluid inclusions at room temperature, typically found in quartz (as shown here) and dolomite veins. Further illustration of fluid inclusions and quartz-dolomite veins, can be found in [Pagel et al., 1980](#); [Kotzer and Kyser, 1995](#); [Derome et al., 2005](#); [Richard et al., 2010, 2011, 2012](#)). For an example of quartz-dolomite vein in mineralized samples see detailed description of sample MAC5 in [Derome et al. \(2005\)](#), referred as sample H459-33.

River ([Derome et al., 2005](#)). However, their interpretation in term of trapping temperature is subjected to assumptions

on: (i) the pressure regime (hydrostatic vs. lithostatic), (ii) possible post-trapping deformation and (iii) possible influence of radiolytic gases (H_2 , O_2). This results in large uncertainty on the actual P - T conditions of the brines at the time of trapping and it has been proposed that the temperature of the brines was between 110 and 220 °C ([Derome et al. 2005](#); [Richard et al., submitted for publication](#)).

3. ANALYTICAL METHODS

3.1. Analysis of quartz and dolomite veins

The analysis of major and trace elements in dolomite samples was performed on dolomite separates obtained by hand picking under the binocular microscope. Fine powders were obtained by crushing in an agate mortar. Powders were analysed at the SARM laboratory (CRPG-CNRS, Nancy, France). Chemical compositions of dolomite powders (300 mg) were obtained, after $LiBO_2$ fusion and dissolution by HNO_3 , by inductively coupled plasma-optical emission spectroscopy (ICP-OES) for major elements and inductively coupled plasma-mass spectrometry (ICP-MS) for trace elements ([Table 2](#)) following the method of [Carignan et al. \(2001\)](#). Detection limits and analytical uncertainties are given in [Table 2](#).

The oxygen isotope composition of quartz was analyzed at the stable isotope laboratory of Géosciences (University of Rennes 1, France). Pure quartz grains were separated by handpicking under a binocular microscope and ground in a boron carbide mortar. In order to remove O_2 from quartz, about 6–7 mg of quartz powder were reacted overnight with BrF_5 at 670 °C using the methodology of [Clayton and Mayeda \(1963\)](#). O_2 was then converted into CO_2 by reaction with hot graphite. CO_2 was analyzed isotopically using a VG SIRA 10 triple collector mass spectrometer. Values of $\delta^{18}O$ for quartz are reported in standard per mil (‰) notation relative to V-SMOW (Vienna Standard Mean Ocean Water). Analyses were performed on distinct analytical sessions involving two bottles of BrF_5 reagent and the measured $\delta^{18}O$ values were slightly corrected given the specific value obtained on the NBS28 international standard and the in-house A1113 granite standard for each session; the amplitude of $\delta^{18}O$ correction was between +0.19 and +0.46‰. Taking into account standard correction and internal reproducibility, the analytical uncertainty for quartz $\delta^{18}O$ values is $\pm 0.2\text{‰}$ (1σ).

The oxygen and carbon isotope composition of dolomite were analyzed at the stable isotope laboratory of Géosciences (University of Rennes 1, France). Pure dolomite grains were separated by handpicking under the binocular microscope and ground in a boron carbide mortar. CO_2 was extracted from about 10 mg of carbonate powders by reaction with anhydrous phosphoric acid (H_3PO_4) in vessels at 50 °C for 12 h using the methodology of [McCrea \(1950\)](#). CO_2 was then analyzed isotopically using a VG SIRA 10 triple collector mass spectrometer. Values of $\delta^{13}C$ for dolomites are reported in standard per mil (‰) notation relative to V-PDB (Vienna Pee Dee Belemnite). The oxygen isotope composition of dolomites (relative to V-SMOW) was calculated assuming pure dolomitic composition and

Table 2

Major and trace element data on dolomite veins. LOI: loss on ignition.

Eagle Point		P-Patch				Rabbit Lake								McArthur River
H1935-8	ES287-1	P48-3Dol	P53-10	P55-15	P63-6	DDH197-5	RBL11	RBL14	RBL1	RBL2	RBL5	RBL7	RBL9	MAC5
2.53	0.86	0.21	6.56	39.94	1.69	bdl	0.41	bdl	0.53	5.37	bdl	bdl	8.84	1.57
bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
0.10	0.12	bdl	0.61	bdl	0.09	0.06	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
7.34	2.21	2.26	3.00	1.00	2.08	1.04	1.12	2.67	2.81	2.32	1.02	0.95	0.80	3.03
0.32	1.04	0.23	0.70	0.37	0.14	0.06	0.08	0.20	0.20	0.19	0.07	0.06	0.04	0.07
16.16	18.58	20.05	18.21	12.51	20.34	21.25	21.02	20.08	19.95	19.11	21.18	21.23	19.50	18.11
28.37	29.90	29.80	27.56	18.29	29.07	29.93	29.92	29.89	29.78	28.06	30.00	30.01	27.61	31.68
bdl	0.08	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
44.09	45.71	46.47	42.76	28.67	45.70	46.31	46.28	46.38	45.79	44.10	46.51	46.50	42.45	44.59
98.92	98.50	99.01	99.45	100.78	99.10	98.64	98.82	99.21	99.06	99.14	98.78	98.74	99.25	99.05
0.82	0.89	0.97	0.95	0.98	1.00	1.02	1.01	0.96	0.96	0.98	1.01	1.02	1.01	0.82
bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
1.96	1.47	bdl	0.49	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
38.47	46.46	42.28	20.56	27.70	57.33	30.18	28.11	26.36	25.70	16.72	38.20	39.69	20.79	59.73
11.68	14.15	bdl	9.88	2.63	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	2.58	bdl
1.82	1.03	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
42.42	62.92	9.97	27.12	15.59	15.38	10.72	12.81	19.57	19.70	9.66	39.15	36.47	10.32	bdl
bdl	bdl	5.26	4.98	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
0.05	0.04	0.03	0.11	bdl	bdl	0.03	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
0.43	0.14	0.32	0.11	bdl	0.10	0.13	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.19
0.07	0.04	0.05	0.02	bdl	0.02	0.01	0.02	0.02	bdl	0.02	0.02	0.01	bdl	0.02
0.21	0.06	0.06	0.08	0.20	0.57	0.10	0.07	0.06	0.12	0.09	bdl	bdl	bdl	bdl
0.41	0.87	152.50	0.31	3.04	0.99	0.35	1.59	0.62	0.16	0.34	12.91	12.78	0.56	16.35
1.07	bdl	2.06	1.20	4.48	4.04	bdl	bdl	2.18	bdl	bdl	1.38	1.55	bdl	81.65
3.69	1.90	2.09	1.96	3.10	6.17	19.62	27.14	15.31	32.29	13.21	5.22	4.50	4.67	2.14
bdl	bdl	8.10	8.38	7.20	5.12	bdl	5.96	6.72	bdl	5.96	5.20	5.07	6.66	117.70
bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
bdl	bdl	bdl	bdl	2.09	bdl	bdl	1.53	bdl	bdl	bdl	bdl	bdl	0.48	75.81
0.86	0.63	1.60	3.25	3.43	3.86	1.12	3.04	7.98	2.91	6.31	2.03	2.66	1.52	92.75
bdl	11.75	139.50	15.80	30.59	7.56	22.42	bdl	10.06	bdl	316.60	125.80	93.60	7.65	22.36
bdl	bdl	bdl	bdl	bdl	bdl	34.83	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
0.64	1.49	bdl	1.57	0.37	bdl	0.31	0.48	bdl	bdl	bdl	bdl	bdl	bdl	bdl
bdl	bdl	0.37	bdl	0.18	0.34	0.17	0.76	0.85	1.13	0.58	bdl	bdl	bdl	bdl
0.13	0.17	bdl	0.17	0.37	0.14	bdl	bdl	bdl	bdl	0.13	bdl	bdl	0.18	bdl
bdl	bdl	8.45	2.53	4.38	6.22	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	3.95
bdl	bdl	0.10	0.15	1.65	1.17	bdl	1.32	bdl	bdl	bdl	bdl	0.14	0.11	0.44
bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
bdl	bdl	0.65	bdl	0.56	0.69	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
bdl	bdl	0.35	bdl	bdl	0.50	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl

(continued on next page)

Table 2 (continued)

Eagle Point	P-Patch		Rabbit Lake					McArthur River						
	ES287-1	P48-3Dol	P53-10	P55-15	P63-6	DDH197-5	RBL11	RBL14	RBL1	RBL2	RBL5	RBL7	RBL9	MAC5
29.83	77.82	1.71	16.51	1.99	1.21	0.77	0.93	0.73	0.33	0.38	2.00	2.11	0.78	1.77
53.18	153.00	6.12	30.77	6.74	4.58	2.87	3.61	3.73	1.94	1.47	13.47	14.19	2.32	0.31
6.21	16.59	1.00	3.84	1.17	0.77	0.43	0.59	0.67	0.37	0.26	2.64	2.68	0.31	0.03
24.57	59.24	4.73	16.24	5.77	3.80	1.85	2.62	2.94	1.70	1.20	12.34	12.34	1.28	0.08
5.55	10.80	2.30	4.21	2.81	1.88	0.65	0.88	1.51	1.10	0.67	4.21	4.12	0.41	bdll
1.51	5.02	0.87	1.48	0.59	0.58	0.18	0.27	0.45	0.36	0.21	1.17	1.10	0.10	0.01
6.37	9.26	2.81	4.21	3.55	3.06	1.01	1.33	3.14	2.74	1.45	4.92	4.70	0.68	bdll
1.01	1.43	0.44	0.65	0.58	0.55	0.28	0.36	0.76	0.74	0.36	1.28	1.21	0.22	bdll
5.98	8.75	2.10	3.95	2.89	2.89	1.98	2.53	4.23	4.32	2.07	8.26	7.78	1.73	0.01
1.17	1.77	0.31	0.79	0.48	0.49	0.33	0.41	0.65	0.66	0.32	1.27	1.17	0.33	bdll
3.12	5.02	0.76	2.32	1.14	1.18	0.82	1.02	1.49	1.52	0.78	2.91	2.72	0.87	0.01
0.43	0.74	0.11	0.38	0.16	0.17	0.11	0.14	0.21	0.21	0.11	0.40	0.38	0.13	bdll
2.68	5.11	0.82	2.77	1.11	1.20	0.68	1.03	1.48	1.41	0.81	2.85	2.59	0.85	0.01
0.41	0.78	0.13	0.45	0.16	0.18	0.10	0.16	0.21	0.20	0.12	0.42	0.39	0.13	bdll

experimental fractionation coefficients $\alpha_{\text{Dol-CO}_2} = 1.01065$ at 50 °C (Rosenbaum and Sheppard, 1986). During the analytical session, measurements on Prolabo Rennes in-house standard and NBS 19 limestone international standard were used to correct the measured $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values by less than 0.1‰. Taking into account standard correction and internal reproducibility, the analytical uncertainty is better than $\pm 0.1\text{‰}$ for $\delta^{13}\text{C}$ (1 σ) and about $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ (1 σ).

Sr isotope analyses on dolomite samples were carried out at the geochemical laboratory of Géosciences (University of Rennes 1, France). About 10 mg of each powdered sample were dissolved in 2 N cold HCl for one hour. Solutions were then centrifuged, dried and redissolved in 2 N cold HCl for Sr separation using standard chromatographic column cation separation (BioRad AG 50WX8 resin, H^+ form, 200–400 mesh). Total blank was 100 pg and was considered as being negligible. Sr was analyzed isotopically using a Finnigan Mat 252 multi-collector mass spectrometer. During the two analytical sessions, repeated measurements on NBS 987 gave a mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710195 (2 σ , $N = 5$) and the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were adjusted to the standard value of 0.710250 ± 7 .

Nd isotope analysis of dolomite samples were performed at the SARM laboratory (CRPG-CNRS, Nancy, France). 100 to 200 mg of powdered samples were digested in screw-top Savillex® Teflon vials using a 4 ml HNO_3 (sub-boiled, 14 M) and 1 ml HF (ultrapur Seastar, 28 M) mixture on a hot plate (115 °C) for 24–48 h and then slowly evaporated. Subsequently, 4 to 5 ml of concentrated (sub-boiled, 11 M) HCl was added to minimize fluoride formation and the solution was dried again. 2 ml of 2 M HNO_3 were added before Nd separation. Nd was separated and purified using conventional anion exchange methods on columns containing Tru Spec and Ln Spec resins (Pin et al., 1994; Pin and Santos Zalduegui, 1997). Nd isotope compositions were measured on a Micromass Isoprobe multi collector-inductively coupled plasma-mass spectrometer (MC-ICP-MS). Mass fractionation was corrected using an exponential law and $^{146}\text{Nd}/^{144}\text{Nd}$ ratios = 0.72190 as the normalization ratio (Luis et al., 1997). Repeated analysis of an in-house JMC Nd standard yielded a $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.512241 ± 32 (2 σ , $N = 10$) during the analytical session. Procedural blanks were negligible with values below 100 pg.

3.2. Analysis of fluid inclusions

The analysis of hydrogen and carbon isotope compositions of bulk fluid inclusions populations in quartz and dolomite was carried out at the CRPG-CNRS laboratory, Nancy, France. Quartz and dolomite veins were crushed to a grain size of 1–5 mm and separated by handpicking under the binocular microscope to avoid mineral impurities. Quartz and dolomite grains were then heated at 100 °C overnight to remove atmospheric water before analyses. 2–8 g of quartz or dolomite grains were crushed in stainless steel tubes under vacuum at 110 °C. Liberated H_2O and CO_2 were collected in a liquid nitrogen cold trap and non-condensable volatiles (e.g. H_2 , O_2 , CH_4 , and N_2) were

evacuated. This methodology prevents from contamination of H_2O and CO_2 by possible solid bitumen in the dolomite lattice. In order to separate CO_2 from H_2O , the liquid nitrogen trap was replaced by an alcohol + liquid nitrogen slush

trap at -80°C . The liberated CO_2 was trapped in a liquid nitrogen cold trap and the amount of recovered CO_2 was measured in a calibrated volume using a Keller manometer. Then, CO_2 was extracted and analyzed isotopically using a

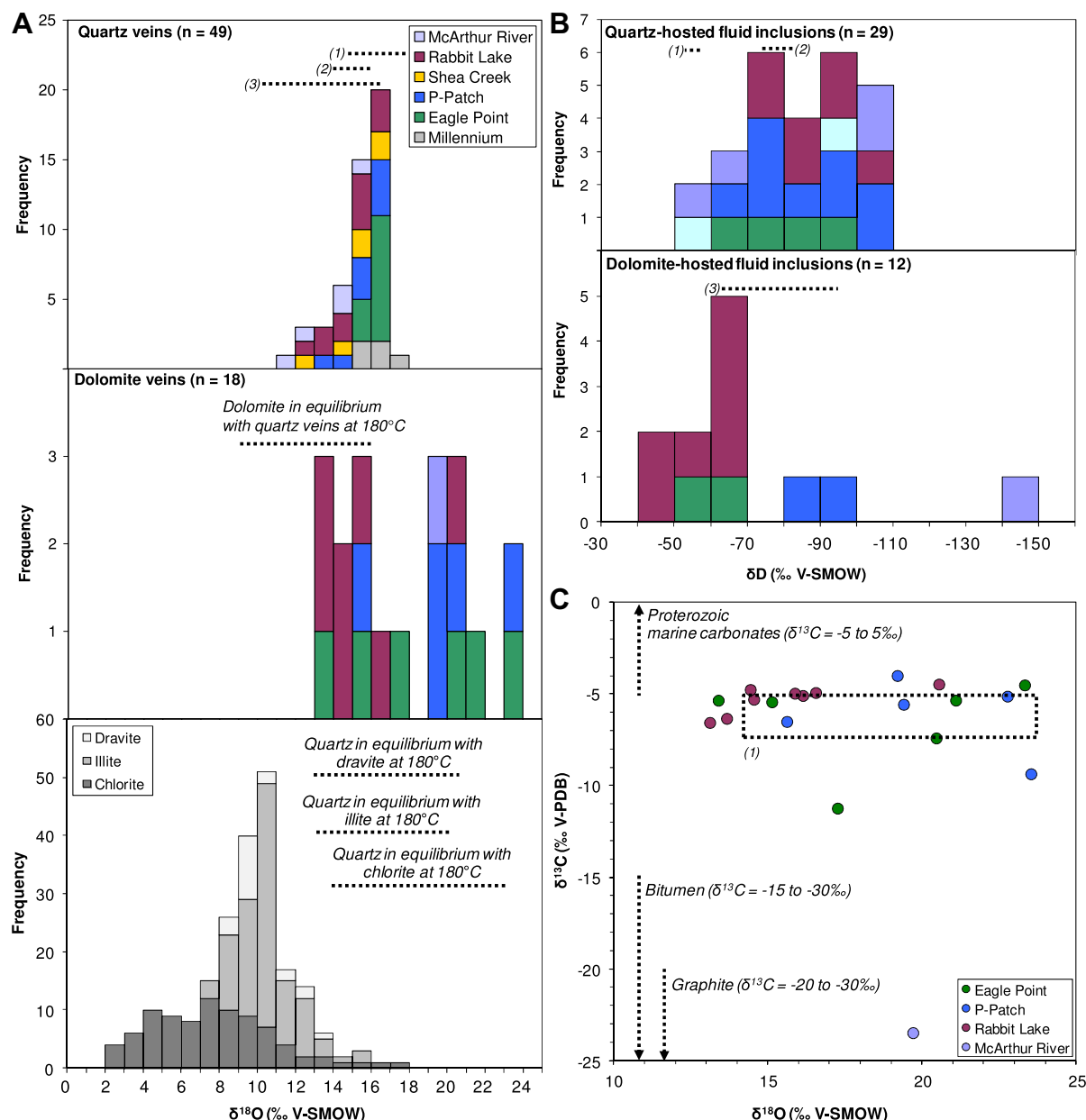


Fig. 3. O, H, C isotope composition of quartz–dolomite veins and their fluid inclusions in the Athabasca Basin and Basement. (A) $\delta^{18}\text{O}$ values of quartz and dolomite veins, compared with the $\delta^{18}\text{O}$ values of alteration minerals (illite, chlorite and dravite) around unconformity-related U deposits in the Athabasca Basin (see Section 5.1.2 for details and source data for alteration minerals). The theoretical $\delta^{18}\text{O}$ values of quartz in isotopic equilibrium with illite, chlorite and dravite at 180°C are indicated (See Section 5.1.2 for fractionation factors). (1) Data from Rabbit Lake ($n = 7$) after Hoeve et al. (1986). (2) Data from Key Lake ($n = 5$) after Wilson and Kyser (1987). (3) Data from McArthur River ($n = 15$) after Kotzer and Kyser (1995). The virtual $\delta^{18}\text{O}$ values of dolomite in isotopic equilibrium with the quartz veins studied here are also indicated (after Zheng, 1993a, 1999). (B) δD of water from quartz- and dolomite-hosted fluid inclusions. (1) Data from McArthur River (number of data not provided) after Kotzer and Kyser (1995). (2) Data from Rabbit Lake ($n = 1$) after Pagel et al. (1980). (3) Data from Rabbit Lake ($n = 3$) after Pagel et al. (1980). (C) $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ diagram for dolomite veins. (1) $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ from Rabbit Lake deposit ($n = 40$) after Pagel et al. (1980) and Hoeve et al. (1986). Field for Proterozoic marine carbonates after Shields and Veizer (2002). $\delta^{13}\text{C}$ range for graphite in Athabasca basement after Wallis et al. (1984) and Kyser et al. (1989). $\delta^{13}\text{C}$ range for bitumen in Athabasca unconformity-related U-ores after Sangély et al. (2007) and Hoeve et al. (1986).

VG Micromass 602D mass spectrometer. Values of $\delta^{13}\text{C}$ for CO_2 are reported in standard per mil (‰) notation relative to V-PDB. Only dolomite grains contained sufficient quantities of CO_2 to be analyzed isotopically. Standard CO_2 samples reproduced to within $\pm 0.1\text{‰}$ (2σ). Owing to the small amounts of recovered CO_2 (typically 1 μmole , molar $\text{H}_2\text{O}/\text{CO}_2 = 30$ to 400), $\delta^{13}\text{C}$ values are given with a rather large uncertainty of $\pm 5\text{‰}$. Water was liberated from the -80°C trap and passed through a U furnace at 800°C where H_2O was reduced to H_2 . H_2 was then pumped using a Toepler pump. The recovery of H_2 from H_2O is assumed to be of 100%. The amount of H_2 was measured in a calibrated volume using a Keller manometer. Then H_2 was extracted and analyzed isotopically using a VG Micromass 602D mass spectrometer. Values of δD for H_2 and thus for fluid inclusions H_2O are reported in standard per mil (‰) notation relative to V-SMOW. When introduced into the same vacuum line with a vacuum-tight micro-syringe, ED3 standard (-60‰) reproduced to within $\pm 2\text{‰}$ (2σ).

4. RESULTS

4.1. Stable isotope (O, C) composition of quartz and dolomite veins

Stable isotope data for quartz and dolomite veins are shown in Table 1 and Fig. 3. They are broadly consistent with those published by Pagel et al. (1980), Hoeve et al. (1986), Wilson and Kyser (1987) and Kotzer and Kyser (1995) for Rabbit Lake, McArthur River and Key Lake deposits.

The $\delta^{18}\text{O}$ values of quartz range between 11.9‰ and 17.4‰ , with 41 values on 49 lying between 14‰ and

17‰ . The highest values are recorded at Millennium and Eagle Point ($\delta^{18}\text{O} = 15.3\text{‰}$ to 17.4‰), intermediate values at P-Patch, Shea Creek and Rabbit Lake ($\delta^{18}\text{O} = 12.9\text{‰}$ to 16.9‰), and the lowest values at McArthur River ($\delta^{18}\text{O} = 11.9\text{‰}$ to 16.0‰). The $\delta^{18}\text{O}$ values of dolomite range from 13.1‰ to 23.8‰ with no clear difference between deposits. Nearly all quartz–dolomite pairs (MAC5, P48-3, RBL14, RLB2, RLB5 and RLB7; Table 1) show isotopic reversal with the $\delta^{18}\text{O}$ value of dolomite being higher than the quartz value (RLB5 is an exception). Also, in Fig. 3A, the dolomite histogram is displaced to the right when compared to the quartz one, which shows that the isotopic disequilibrium between dolomite and quartz is the rule rather than the exception in the Athabasca Basin ore deposits. There is no clear relationship between the $\delta^{18}\text{O}$ value of quartz and dolomite and their sampling depth below unconformity (Table 1).

The $\delta^{13}\text{C}$ values of dolomite range from -23.5‰ to -3.5‰ with a majority of values between -3.5‰ and -8‰ . There is no significant difference between deposits, and the extremely low value of -23.5‰ measured in only one sample from the McArthur River deposit can hardly be considered as representative of the whole site. No correlation is observed between the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of dolomite (Fig. 3C).

4.2. Stable isotope (H, C) composition of fluid inclusions

Hydrogen and carbon isotope data for quartz- and dolomite-hosted fluid inclusions are shown in Table 1 and Fig. 3B and C. The heterogeneity of samples was tested by analyzing two or three separates of individual veins. Replicate analyses show that some samples have quite

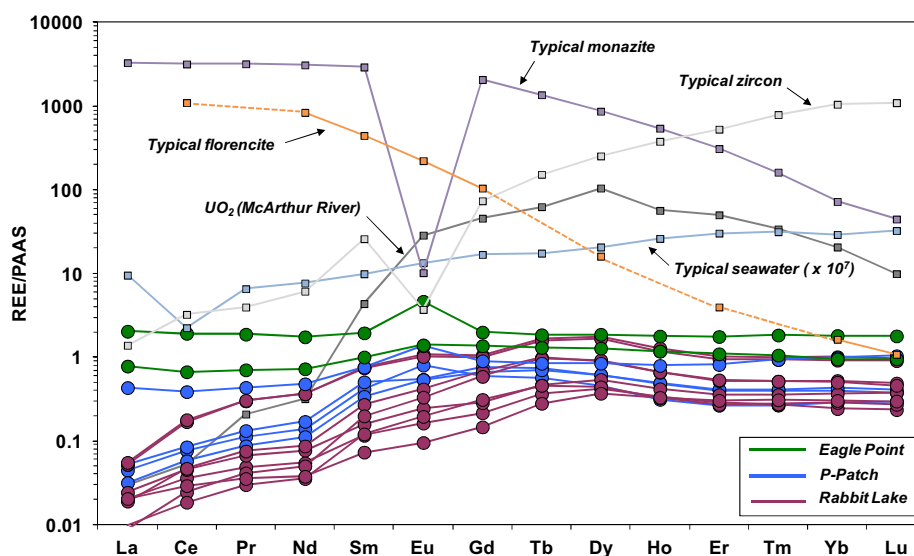


Fig. 4. Rare Earth Element (REE) concentrations in Athabasca dolomite veins and other reference materials (UO_2 , seawater, monazite, zircon, florencite). All data normalized to Post Archean Australian Shales (PAAS). Normalization values are from Taylor and McLennan (1985). Data is not shown for sample MAC5 which has very low REE abundances compared to other samples (see Table 1). Data for Athabasca UO_2 (McArthur River deposit) are indicated for comparison (after Mercadier et al., 2011a). Data for seawater after Zhang and Nozaki (1998); monazite and zircon after Pettke et al. (2005) and florencite (aluminum phosphate–sulphate mineral) after Rasmussen et al. (1998).

Table 3

Rb/Sr and Sm/Nd isotope data for dolomite veins. $^{87}\text{Rb}/^{86}\text{Sr}$ ratios for samples with Rb concentration below 0.3 ppm were calculated using Rb concentration of 0.15 ppm. This results in calculated $^{87}\text{Sr}/^{86}\text{Sr}_i$ values nearly indistinct from the today $^{87}\text{Sr}/^{86}\text{Sr}$. Therefore for these samples $^{87}\text{Sr}/^{86}\text{Sr}_i$ values are not reported. The Nd isotope composition of MAC5 sample was not measured due to insufficient Nd content.

Sample	Rb (ppm)	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr} \pm 2\sigma$	$(^{87}\text{Rb}/^{86}\text{Sr})$	$(^{87}\text{Sr}/^{86}\text{Sr})_i$	Sm (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd} \pm 2\sigma$	$\varepsilon_{\text{Nd}}(t)$
<i>Eagle point</i>										
H1935-8	2.0	38.5	0.718747 ± 0.00001	0.1471	0.7161 ± 0.0005	5.6	24.6	0.1366	0.511542 ± 0.000007	-11.8 ± 1.9
ES287-1	1.5	46.5	0.711050 ± 0.00001	0.0917	0.7094 ± 0.0003	10.8	59.2	0.1102	0.511253 ± 0.000006	-13.2 ± 2.8
<i>P-Patch</i>										
P48-3	<0.3	42.3	0.707945 ± 0.00001	0.0103	0.7083 ± 0.0002	2.3	4.7	0.2940	0.512398 ± 0.000010	-20.3 ± 3.2
P53-10	0.5	20.6	0.709526 ± 0.00001	0.0694		4.2	16.2	0.1568	0.511391 ± 0.000005	-18.0 ± 1.3
P55-15	<0.3	27.7	0.710542 ± 0.00001	0.0157		2.8	5.8	0.2938	0.512251 ± 0.000012	-23.2 ± 3.2
P63-6	<0.3	57.3	0.708407 ± 0.00001	0.0076		1.9	3.8	0.2993	0.512491 ± 0.000010	-19.3 ± 3.3
<i>Rabbit Lake</i>										
DDH197-5	<0.3	30.2	0.705622 ± 0.00001	0.0144	0.7100 ± 0.0002	0.6	1.8	0.2110	0.512206 ± 0.000012	-10.7 ± 0.5
RBL11	<0.3	28.1	0.707559 ± 0.00001	0.0154		0.9	2.6	0.2020	0.512231 ± 0.000017	-8.8 ± 0.2
RBL14	<0.3	26.4	0.707166 ± 0.00001	0.0165		1.5	2.9	0.3111	0.512810 ± 0.000016	-15.0 ± 3.7
RBL1	<0.3	25.7	0.706697 ± 0.00001	0.0169		1.1	1.7	0.3923	0.513774 ± 0.000030	-9.2 ± 6.3
RBL2	<0.3	16.7	0.706810 ± 0.00001	0.0260		0.7	1.2	0.3372	0.513047 ± 0.000010	-14.6 ± 4.5
RBL5	<0.3	38.2	0.705296 ± 0.00001	0.0114		4.2	12.3	0.2063	0.512138 ± 0.000007	-11.3 ± 0.3
RBL7	<0.3	39.7	0.705418 ± 0.00001	0.0109		4.1	12.3	0.2016	0.512152 ± 0.000007	-10.3 ± 0.2
RBL9	<0.3	20.8	0.705751 ± 0.00001	0.0209		0.4	1.3	0.1925	0.512062 ± 0.000013	-10.6 ± 0.1
<i>McArthur River</i>										
MAC5	<0.3	59.7	0.709962 ± 0.00001	0.0073		0.01	0.1			

reproducible δD values ($\pm 2\text{‰}$) while other samples display larger variability ($\pm 10\text{‰}$), as noted by Pagel et al. (1980) for comparable measurements on Rabbit Lake samples. The δD values reported in Table 1 correspond to the average value among two or three replicate analyses. Therefore, a conservative uncertainty of $\pm 10\text{‰}$ was applied to all δD values. This high internal variability is well beyond analytical reproducibility ($\pm 2\text{‰}$; 2σ) and is attributable to heterogeneities at the scale of individual veins. A minor influence of phyllosilicate daughter phases in fluid inclusions cannot be ruled out. Heterogeneities at the scale of individual veins may also account for the variability of the $\delta^{13}C$ values which are given with a conservative uncertainty of $\pm 5\text{‰}$.

The δD values of quartz-hosted fluid inclusions range from -52‰ to -110‰ (predominantly above -70‰). The δD values of dolomite-hosted fluid inclusions range from -46‰ to -147‰ (predominantly above -70‰). The new data presented here compare broadly to the few published data from Pagel et al. (1980) and Kotzer and Kyser (1995) for Rabbit Lake dolomite and McArthur River quartz respectively (Fig. 3B). For Eagle Point and Rabbit Lake deposits, the δD values of dolomite-hosted fluid inclusions are higher than for quartz-hosted fluid inclusions. The reverse relationship is observed for McArthur River deposit. At P-Patch, δD values of dolomite-hosted and quartz-hosted fluid inclusions overlap. Combined with the fact that the number of data is rather small for each deposit, it can be concluded that there is no general rule for discrimination of δD values between dolomite-hosted and quartz-hosted fluid inclusions. In veins where both quartz and dolomite precipitated, the δD values of quartz-hosted and dolomite hosted fluid inclusions differ significantly. Generally, the δD value of quartz-hosted inclusions is below that of dolomite-hosted inclusions, the two exceptions being samples P48-3 and MAC5. The δD values of fluid inclusions and the $\delta^{13}C$ values of CO_2 do not show any relationship to depth below unconformity. No CO_2 was recovered from quartz veins whereas small amounts of CO_2 were recovered from dolomite veins (see Section 3.2). This explains why, in spite of their differences in their CO_2 content, no CO_2 was detected in dolomite-hosted fluid inclusions during microthermometry and quartz- and dolomite-hosted fluid inclusions show similar microthermometric characteristics. The $\delta^{13}C$ values of CO_2 dissolved in dolomite-hosted fluid inclusions are mostly between -8‰ and -19‰ with two noticeable exceptions at -4‰ (sample RBL14) and -30‰ (sample MAC5). Interestingly, the lowest $\delta^{13}C$ values of CO_2 and dolomite, corresponds to the lowest δD value (sample MAC5).

4.3. Chemical composition of dolomite veins

Chemical compositions are reported in Table 2. The Mg/Ca molar ratio is most often close to unity and indicates pure dolomite, except in Eagle Point and McArthur River samples where a minor ankeritic component is present. Also, some samples contain a significant amount of quartz (samples P55-15, RLB2 and RLB9), with an associated dilution of trace element contents hosted in dolomite (Sr). The U content of dolomite veins is up to 16 ppm in

sample MAC5 and 152 ppm in sample P48-3, possibly due to tiny U-bearing mineral inclusions. Interestingly, these two samples have also the lowest δD values of fluid inclusions. The Sr content is between 16 and 60 ppm, which corresponds to classical contents for dolomites. The Rb content is consistently very low, generally below the detection limit (bld) (maximum = 1.96 ppm, sample H1935-8). Some elements show variable content, for example Cu between bld and more than 300 ppm (sample RBL2). Noteworthy P-Patch samples are enriched in As (between 2 and 8 ppm). Variable Cu and As contents are possibly attributable to sulphide mineral inclusions.

Fig. 4 shows the PAAS-normalized REE spectra of dolomite. The REE patterns of dolomite samples are homogeneous, with LREE depleted patterns, a generally upward convex pattern and flat HREE pattern close to the PAAS abundance. Three samples display relatively flat REE patterns and positive Eu anomaly. The first group of dolomite displays a tetrad effect pattern. Sample MAC5 has very low REE content below the detection limit for most REE (Table 2; not shown in Fig. 4).

4.4. Radiogenic isotope (Sr, Nd) composition of dolomite veins

The Sr isotope composition of dolomite (Table 3) is rather homogeneous between 0.705 and 0.711, with sample H1935-8 displaying a more radiogenic composition of 0.718. $^{87}Sr/^{86}Sr$ initial ratios were calculated at $t = 1250 \pm 250$ Ma, which covers the most probable ages of U mobilization and precipitation of dolomite in the Ath-

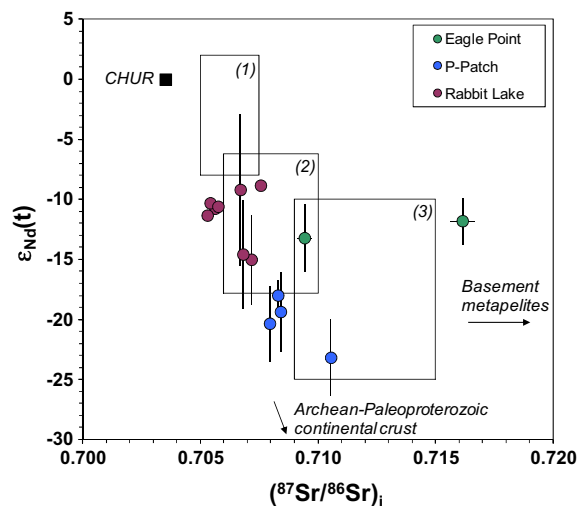


Fig. 5. Sr and Nd isotope compositions of the Athabasca dolomite veins. $^{87}Sr/^{86}Sr_i = ^{87}Sr/^{86}Sr$ for samples with Rb < 0.3 ppm (see Table 3). Compositional fields for reservoirs of interest have been reconstructed after data from various localities in the Athabasca basin and basement: (1) Proterozoic seawater (Derry and Jacobsen, 1988; Veizer, 1989); (2) Athabasca sandstones (Manitou Falls and Wolverine Point formations, Kotzer and Kyser (1995), Armstrong and Ramaekers (1985), Pagel et al. (1993)); (3) UO_2 Fryer and Taylor (1984), Carl et al. (1992), Pagel et al. (1993), Fayek and Kyser (1997); Basement metapelites (Pagel et al., 1993).

Abasca system (Cumming and Krstic, 1992; Fayek et al., 2002; Alexandre et al., 2009a). These Sr initial isotope ratios are not very different from present-day ratios because of the very low Rb content of dolomite. At 1250 ± 250 Ma, the Nd isotope composition of dolomite varies much more than the Sr isotope ratios as the $\varepsilon_{\text{Nd}}(t)$ value is between -8.8 and -20.3 . The data from the three studied deposits plot in distinct fields (Fig. 5) and $^{87}\text{Sr}/^{86}\text{Sr}_i$ and $\varepsilon_{\text{Nd}}(t)$ values show no clear relationship with each other or with another isotopic system, for a given deposit. Removing sample H1935-8 from the whole database, it is however possible to identify a negative correlation between the two isotopic compositions.

5. DISCUSSION

5.1. Quartz–dolomite veins in the mineralizing process

5.1.1. Quartz–dolomite isotopic disequilibrium and temperature variation

Microthermometric data on fluid inclusions do not provide better estimate than the range 110 – 220 °C for the temperature of quartz and dolomite precipitation (see Section 2.4). Also, chemical data on quartz- and dolomite-hosted fluid inclusions indicate that both minerals equilibrated with comparable brines.

Fig. 3A shows the theoretical $\delta^{18}\text{O}$ value of dolomite in isotopic equilibrium at 180 °C (as a working hypothesis) with the quartz veins. The dolomite with $\delta^{18}\text{O} > 19\text{‰}$ could not be equilibrated with the quartz veins, as also shown in veins where both quartz and dolomite precipitate (see Section 4.1). Instead, the high $\delta^{18}\text{O}$ value of dolomite indicates mineral precipitation at lower temperature or from a higher $\delta^{18}\text{O}$ fluid (or a combination of both). Two arguments plead for a temperature decrease. First, a lower temperature event is consistent with paragenetic observations because dolomite crystals generally formed later than quartz in veins (Fig. 2C and D) and thus at lower temperature in a cooling system. Second, the brine from which dolomite formed resembles the one from which quartz did, which implies that on a first order, the $\delta^{18}\text{O}$ value of the fluid was comparable in both cases and that only a temperature decrease for the dolomite stage can explain the high $\delta^{18}\text{O}$ value of this mineral. As a crude estimate, the isotopic difference between quartz and part of the dolomite ($\delta^{18}\text{O} > 19\text{‰}$) may indicate a temperature of precipitation decrease of ~ 50 – 100 °C within the 110 – 220 °C range defined by fluid inclusion microthermometry.

Consistently, when considering the uncertainty on $\delta^{13}\text{C}$ values of CO_2 , most $\delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{Dol}}$ pairs indicate apparent temperature of dolomite crystallization (and fluid inclusion trapping) ranging between 50 and 150 °C (Ohmoto and Rye, 1979). Although this is a crude estimate, this is consistent with the idea that dolomite precipitation documents a lower temperature event than the quartz stage.

Dolomite precipitation during cooling is at variance with the theoretical increase of dolomite solubility with cooling (Bertram et al., 1991; Burton and Walter, 1991; Warren, 2000; Lopez et al., 2009). Cooling was not responsible by itself for dolomite precipitation. Precipitation of

hydrothermal dolomite from Na–Ca–Mg brines at comparable temperatures is well documented in sedimentary environments (e.g. Gleeson and Turner, 2007; Conliffe et al., 2010; Gromek et al., 2012). Dolomite precipitation is partially controlled by the Ca/Mg content of the fluids. Here, microthermometrically similar fluid inclusions do not suggest drastic change in Ca/Mg during the quartz and the dolomite stages. Subtle changes in Ca/Mg would however be difficult to identify by microthermometry only due to comparable phase relationships between the H_2O – NaCl – CaCl_2 and H_2O – NaCl – MgCl_2 systems (Dubois and Marinac, 1997; Steele-MacInnis et al., 2011). In addition, Mg and Ca in dolomite-hosted fluid inclusions cannot be determined by LA-ICP-MS due the high Ca and Mg content of the host mineral. An independent factor of dolomite precipitation is thus necessary and might be found in the increase in partial pressure of CO_2 ($p\text{CO}_2$) in the fluid phase, which is documented by the recovery of CO_2 in dolomite-hosted fluid inclusions.

5.1.2. Isotopic equilibrium between quartz and alteration minerals

Fig. 3A shows a compilation of the published $\delta^{18}\text{O}$ values of the main alteration minerals paragenetically associated with U ores throughout the Athabasca Basin (illite, chlorite and dravite). Only the $\delta^{18}\text{O}$ values of pure illite, chlorite and dravite separates have been considered here; they have been compiled from the following sources: Pagel et al. (1980), Hoeve et al. (1986), Halter et al. (1987), Wilson et al. (1987), Bray et al. (1988), Kotzer and Kyser (1991, 1995), Percival et al. (1993), Alexandre et al. (2005, 2009b) and Cloutier et al. (2009, 2010, 2011). The $\delta^{18}\text{O}$ values of chlorite are highly variable (2 – 18‰) but with very few values above 12‰ . The $\delta^{18}\text{O}$ values of illite and dravite range from 8‰ to 13‰ . The theoretical range of $\delta^{18}\text{O}$ values of quartz in isotopic equilibrium with the alteration minerals at 180 °C was calculated using the fractionation factors of Wenner and Taylor (1971), Eslinger and Savin (1973), Kotzer et al. (1993) and Zheng (1993a,b). Several issues arise from this data compilation. The spread of $\delta^{18}\text{O}$ values of alteration minerals goes well beyond simple temperature variation effects if the $\delta^{18}\text{O}$ of the fluid remains nearly constant. The $\delta^{18}\text{O}$ values of quartz show a pronounced skew to low values that would indicate unreasonably high temperature if quartz was isotopically equilibrated with alteration minerals. Further work is needed on carefully selected alteration mineral + quartz assemblages to solve these problems. In spite of these uncertainties, the isotopic composition of quartz veins analyzed here compares rather well with the calculated isotopic composition of quartz at isotopic equilibrium with alteration minerals at 180 °C (Fig. 3A). This calculation shows that quartz veins and alteration minerals are in global isotopic equilibrium near 180 °C and therefore likely belong to a single event of alteration.

5.1.3. Genetic link between dolomite and UO_2

Besides UO_2 , the main REE-bearing minerals in the vicinity of the studied deposits are monazite and zircon. During hydrothermal alteration, Hecht and Cuney (2000),

Fayek and Kyser (1997), Gaboreau et al. (2007) and Mercadier et al. (2011a) have proposed that the REE were redistributed from monazite and zircon to aluminum phosphate–sulfate minerals (APS) and UO_2 . In Fig. 4 the REE spectra of dolomite are clearly distinct from those of typical seawater, monazite, zircon and APS (florencite). The REE upward convex patterns with tetrad effects are comparable in shape to those of UO_2 grains from the McArthur River deposit (Mercadier et al., 2011a), the main if not the only difference being the enrichment in MREE and HREE. In the UO_2 , the major enrichment compared to PAAS is centered on Dy, the element most readily incorporated in the UO_2 crystal structure. Thus, it has been inferred that the REE patterns reflect differences in partition coefficients between UO_2 and a single fluid phase (Mercadier et al., 2011a). Here, major enrichment centered on Dy is also observed in dolomite and cannot be related to possible tiny UO_2 inclusions in dolomite lattice because the U and REE contents of dolomite are not correlated (Table 1). By consequence, some particularities of the REE patterns may be partly representative of the fluid itself (i.e. LREE depletion, tetrad effect, enrichment centered on Dy and flat HREE patterns). These results highlight that dolomite and UO_2 incorporated REE from a similar source, even if UO_2 slightly predated dolomite precipitation in the paragenetic sequence. This idea is consistent with the comparable Nd isotope signature of the two minerals ($\varepsilon_{\text{Nd}}(-t)$ between -10 and -25). The very low REE content in sample MAC5 (not shown in Fig. 4) could be related to massive incorporation of REE within UO_2 , a process that would be specific to the very high-grade, large tonnage McArthur River deposit.

In Fig. 5, the overall negative correlation visible excluding the high $^{87}\text{Sr}/^{86}\text{Sr}$ sample (sample H1935-8 from Eagle Point) can be classically interpreted as a mixing hyperbola involving at least two sources, one encountered in the Archean basement, the other one being Proterozoic seawater (from which the mineralizing brines ultimately originate). In this context, the large variation in $\varepsilon_{\text{Nd}}(t)$ value in most dolomite veins when compared to the variation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio may be related to the higher Sr content of brines. Indeed, when brines interact with basement rocks, they are more able to keep their original Sr signature rather than their Nd one given that $(\text{Sr}/\text{Nd})_{\text{brine}} \gg (\text{Sr}/\text{Nd})_{\text{basement}}$. The UO_2 data locate at the lower right side of the dolomite field and have isotopic compositions closer to host basement rocks (Archean basement and local gneiss). It seems then that the brines at the origin of the UO_2 stage interacted to some more extent with basement rocks than the one related to the dolomite stage.

Sample H1935-8 has a peculiar position with regard to the whole dolomite population, but it clearly points to a major contribution of the local gneiss in its Sr isotope composition, as does the other sample from Eagle Point (ES-287-1) to a lesser extent. Also, the fact that the dolomite population of each deposit has distinct Sr and Nd isotope compositions likely indicates that each population records distinct fluid–rock interactions characteristics, in terms of fluid/rock ratios and possibly the nature of the rocks with which brines interacted (i.e. local heterogeneities in the

basement). Qualitatively, this could possibly indicate that the dolomite stage resulted from small (or local) scale fluid movement, whereas the UO_2 stage may have resulted from some larger (or regional) scale fluid movement. Such a decrease of scale of fluid circulation is consistent with the lowering of the temperature between the quartz precipitation stage (synchronous with UO_2 precipitation) and the dolomite stage.

5.2. Evolution of brines through alteration and mineralization

5.2.1. Reconstruction of the O isotope composition of brines

Calculating the $\delta^{18}\text{O}$ values of brines is possible only if the precipitation temperature of quartz and dolomite is known. Here, microthermometric data indicate temperatures of 110 – 220 °C (Derome et al., 2005; Richard et al., submitted for publication) and oxygen isotope data indicate 50 – 100 °C of temperature difference for crystallization between quartz and part of dolomite veins ($\delta^{18}\text{O} > 19\text{‰}$; See Section 5.1.1). Quartz and alteration minerals are isotopically equilibrated at around 180 °C (Fig. 3A; see Section 5.1.2). Hence, a reasonable working hypothesis is that the dolomites with $\delta^{18}\text{O} > 19\text{‰}$ have precipitated at temperature possibly around 120 °C while dolomites with $\delta^{18}\text{O} < 19\text{‰}$ have precipitated at higher temperatures, possibly up to 180 °C. At these temperatures, the fractionation factors of Zheng (1993a) and Zheng (1999) are used to calculate the $\delta^{18}\text{O}$ value of fluids in equilibrium with quartz and dolomite by correcting minerals $\delta^{18}\text{O}$ value by -13.0‰ for quartz, -11.2‰ for dolomite precipitating at 180 °C and -16.1‰ for dolomite precipitating at 120 °C. A bulk uncertainty, taking into account analytical precision and an uncertainty of ± 30 °C for temperature, is estimated at $\pm 2.5\text{‰}$ for the $\delta^{18}\text{O}$ values of brines. Also, the effect of dissolved salts on mineral– H_2O fractionation (the so-called ‘salt-effect’) was estimated according to the regression of experimental data summarized in Chacko et al. (2003). This effect is dependent on the temperature of mineral precipitation, and amount of each dissolved major salts (NaCl, KCl, CaCl_2 , MgCl_2). Using the amount of major salts from Richard et al. (2010), the isotopic data should be corrected by $+0.4\text{‰}$ and $+1.1\text{‰}$ for the veins that precipitated from a NaCl-rich brine and a CaCl_2 -rich brine, respectively. Because most samples have precipitated in the presence of mixtures the two brines, an average salt correction of $+0.7\text{‰}$ was applied to all samples. The reconstructed $\delta^{18}\text{O}$ values of the mineralizing brines are reported in Fig. 6, together with the δD measurement on fluid inclusions.

5.2.2. Evidence for O, H isotope modifications

In Fig. 6, the position of present-day seawater and meteoric water line is reported for reference, as it is for other publications dealing with O and H isotope compositions in the Athabasca context (e.g. Wilson et al., 1987; Kotzer and Kyser, 1995), regardless of the debate as to whether such values are appropriate for the geological past (Lécuyer et al., 1996; Jaffrés et al., 2007; Pope et al., 2012). Displacing seawater composition within the possible range of its inferred past variations would induce a displacement of the star symbol figuring the parent brine from which the miner-

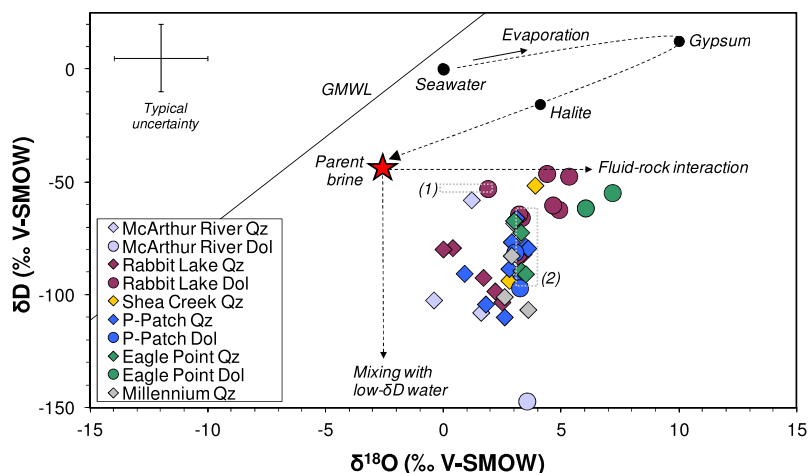


Fig. 6. δD vs. $\delta^{18}O$ for fluid inclusion water in Athabasca quartz (diamonds) and dolomite (circles) veins. $\delta^{18}O$ values for fluid inclusion water were calculated assuming host mineral precipitation occurred at 180 °C (quartz and dolomite with $\delta^{18}O < 19\text{‰}$) and 120 °C (dolomite with $\delta^{18}O > 19\text{‰}$) (see Section 5.2.1 for details on reconstruction of $\delta^{18}O$ values). Seawater evaporation trend after Holser (1979) and Knauth and Beeunas (1986). GMWL: Global meteoric water line. (1) Representative fluid inclusion data from McArthur River quartz veins after Kotzer and Kyser (1995) ($\delta^{18}O$ values calculated from $\delta^{18}O$ values of host quartz at 180 °C). (2) Fluid inclusion data from Rabbit Lake dolomite veins after Pagel et al. (1980) ($\delta^{18}O$ values calculated from $\delta^{18}O$ values of host dolomite at 180 °C).

alizing brines evolved, but would not affect the body of evidence for O, H isotopic modifications as well as the internal variation of the present dataset. This isotopic dispersion is discussed below.

In the present dataset $\delta^{18}O$ – δD pairs are not available for all samples. There is no clear difference between deposits. The reconstructed compositions compare rather well with the few compositions available using the same methodology from McArthur River quartz (Kotzer and Kyser, 1995) and Rabbit Lake dolomite (Pagel et al. 1980) (Fig. 6). As already depicted in the result section, it is apparent that some dolomite-hosted brines yield higher δD values than the corresponding quartz (see Rabbit Lake deposit for example). Many factors can account for the (O, H) composition of the brines.

Cl/Br ratios and stable chlorine isotope compositions have shown the NaCl and $CaCl_2$ -rich brines originate from a common ‘parent brine’ derived from seawater evaporation beyond halite saturation (Derome et al., 2007; Richard et al., 2011; Leisen et al., 2012). In order to compare the composition of the brines from which quartz–dolomite veins have precipitated with the evaporated seawater from which they originate, the seawater evaporation trend was plotted in Fig. 6 (Holser, 1979; Knauth and Beeunas, 1986). Assuming that seawater was evaporated up to epsomite saturation the residual brine would have $\delta^{18}O$ and δD values of $\sim -3\text{‰}$ and $\sim -40\text{‰}$ respectively.

As a whole, the calculated brine compositions are located on the lower right side of the Global Meteoric Water Line, and are clearly distinct from the composition of the parent brine (Fig. 6). Compared to the parent brine, $\delta^{18}O$ and δD values have been shifted by $+2\text{‰}$ to $+10\text{‰}$ and -5‰ to -100‰ respectively. Note that even though the exact temperatures of precipitation of quartz and dolomite are not precisely constrained by fluid inclusions (Derome et al., 2005), a positive $\delta^{18}O$ shift is found for the whole

range of temperature invoked (110–220 °C). Considering the uncertainties on the $\delta^{18}O$ value of the parent brine and on the temperature of quartz and dolomite precipitation, the magnitude of the positive shift ($+2\text{‰}$ to $+10\text{‰}$) should be considered as a guideline.

Although a positive $\delta^{18}O$ shift is expected in the context of intense fluid–rock interaction, one striking feature is the magnitude of δD shift compared to the parent brine. The δD values below -90‰ are comparable to those of organic water (i.e. water derived from reaction involving organic matter, Sheppard, 1986). Anomalously low δD fluids have been reported in a variety of geological environments (Gleeson et al. (1999) and references therein) and a controversy has emerged on the significance of low δD values measured on bulk fluid inclusion populations, alternatively interpreted as reflecting geological processes (e.g. mixing with organic waters, membrane filtration, see Gleeson et al. (1999) for review), or experimental artefacts (i.e. mixing between fluid inclusion water and structurally bound water) (Simon, 2001; Gleeson et al., 2008). However, mechanical crushing at temperature below 200 °C appears to be a reliable method for δD analysis of bulk fluid inclusion population (Simon, 2001) which supports that δD values presented here reflect the original δD composition of the brines. In addition, during the experiments, there was no observed relationship between the δD value and the amount of water liberated relative to the amount of crushed mineral (typically 0.005 to 0.05 $\mu\text{mol}/\text{mg}$), meaning the potential contribution of isotopically light structurally bound water is negligible.

5.2.3. Origin of O isotope modifications

One classical explanation for positive $\delta^{18}O$ shifts in hydrothermal waters is fluid–rock interaction (Williams and McKibben, 1989). In the present work, positive $\delta^{18}O$ shifts between evaporated seawater and the brines ($+2\text{‰}$

to +10‰, Fig. 6) could alternatively be caused by diagenetic processes in the Athabasca Basin or fluid–rock interactions in the basement, under low fluid/rock ratio conditions. By contrast, the intense alteration observed around unconformity-related U deposits (see Section 2.2) is more typical of high fluid–rock ratios (Lorilleux et al., 2003).

Large variations in Na–Ca–Mg composition in the NaCl- and CaCl₂-rich brines (Richard et al., 2010) can be attributed to either albitization of plagioclase or dolomitization reactions (Davisson and Criss, 1996; Houston et al., 2011). Assuming a $\delta^{18}\text{O}$ value of 10‰ for plagioclase and initial $\delta^{18}\text{O}$ value of –3‰ for the evaporated seawater, significant positive $\delta^{18}\text{O}$ shifts (>2‰) due to albitization of plagioclase by evaporated seawater is only possible at temperatures above 150 °C and a $\delta^{18}\text{O}$ shift of +6‰ is only possible at 350 °C (Zheng, 1993a) which is unreasonably high for the studied brines. Detrital plagioclase grains are nearly absent from the preserved sedimentary succession (Ramaekers et al., 2007) and albitization of basement plagioclase has not been observed (Mercadier et al., 2010). Hoeve and Sibbald (1978) mentioned the occurrence of albite-rich plagioclase at Rabbit Lake, although their formation appears to be disconnected (anterior) to brine circulation. Therefore even though albitization is a plausible cause for the high Ca/Na in the CaCl₂-rich brine, such a reaction hardly accounts for most of the positive isotopic shift. Similarly, the widespread illitization and chloritization of feldspar and biotite in basement rocks (Mercadier et al., 2010) cannot be the unique cause for isotopic shift, considering that most of these alteration minerals (illite, chlorite) have $\delta^{18}\text{O}$ values close to 10‰ (Fig. 3A). Assuming a $\delta^{18}\text{O}$ value of 30‰ for marine calcite and initial $\delta^{18}\text{O}$ value of –3‰ for the evaporated seawater, dolomitization of calcite would readily produce residual fluids with $\delta^{18}\text{O}$ value up to 10‰ (Zheng, 1993a) in the range of temperature relevant to this study (25–200 °C). Stromatolitic to massive dolostones are described in the Carswell Formation (Ramaekers et al., 2007) although the conditions for dolomitization have not been studied. Interaction with dolomitic marbles in the basement (Annesley et al., 2005) is one possibility of acquiring heavy O isotopic composition. Such a lithology has been recognised and has $\delta^{18}\text{O}$ values of 12–18‰ at Rabbit Lake (Hoeve et al., 1986). Finally, mass balance considerations suggest that the presence of some healed microfractures in quartz and dolomite (see Section 2.2) could not attest for significant modification of the primary O isotope composition of the host minerals.

Hence, further work is needed in order to specify the exact process responsible for the positive $\delta^{18}\text{O}$ shift in the mineralizing brines. However, the results show that the mineralizing brines have strongly re-equilibrated with host rocks at low fluid–rock ratios and distal to alteration haloes.

5.2.4. Origin of CO₂

Alteration of graphite in basement metasediments is widespread in the vicinity of U deposits of the Athabasca Basin and is spatially related to reactivated fault systems where brine circulations were the most intense. This alter-

ation results in partial to complete dissolution and remobilization of graphite along faults (Kyser et al., 1989; Wang et al., 1989). Hoeve and Sibbald (1978) proposed that CH₄ was the dominant product of brine–graphite interaction. Bray et al. (1988) proposed that interaction of brines with graphitic metasediments could have produced CO₂ ± CH₄ ± H₂S ± H₂ gases. They suggested that CO₂ was the dominant product of graphite alteration based on gas chromatographic analysis of heated illitic and chloritic material. Hoeve and Sibbald (1978) and Bray et al. (1988) both suggested that the migration of gases (especially CH₄) produced by brine–graphite interaction was a viable process for the reduction of U(VI) to U(IV) and subsequent UO₂ deposition. Based on $\delta^{13}\text{C}$ measurements on unaltered and altered graphite, Kyser et al. (1989) concluded that CO₂ was also the dominant product of brine–graphite interaction, well beyond CH₄. Considering $\delta^{13}\text{C}$ composition of graphite ranging from –30‰ to –20‰ (Kyser et al., 1989; Wallis et al., 1986), and by using fractionation factors for graphite–CO₂ isotopic equilibrium (Ohmoto and Rye, 1979), CO₂ in equilibrium with graphite resulting from brine–graphite interaction at 120–180 °C would have $\delta^{13}\text{C}$ values of ~ –15 to –5‰. Thus, the $\delta^{13}\text{C}$ values of dolomites and CO₂ dissolved in dolomite-hosted fluid inclusions are consistent with brine–graphite interaction at 120–180 °C as the origin of CO₂ in the studied brines. In addition samples MAC5 and P48-3 display the lowest δD and $\delta^{13}\text{C}$ values of fluid inclusions in dolomites. This suggests a possible link between C and H isotopic compositions.

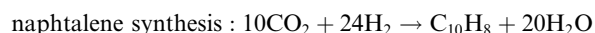
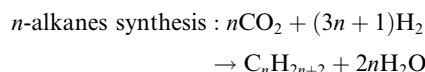
5.2.5. Origin of H isotope modifications

The δD values of the main alteration minerals (illite, sudoite, dravite, kaolinite) have been extensively studied in the Athabasca system (Wilson and Kyser, 1987; Bray et al., 1988; Kotzer and Kyser, 1995; Alexandre et al., 2005, 2009b; Cloutier et al., 2009, 2010, 2011). In most works, the δD values were interpreted in terms of involvement of a basin-derived fluid ($\delta\text{D} = -40\text{‰}$ to -70‰) and a basement-derived fluid (0‰ to -70‰). A controversy has emerged from some extremely low δD values ($\delta\text{D} < -70\text{‰}$) which were alternatively explained by: (1) primary equilibration with low δD fluids (Pagel et al., 1980; Bray et al., 1988); (2) radiation-catalyzed hydrogen exchange (Halter et al., 1987) or (3) late re-equilibration with meteoric waters (Wilson and Kyser, 1987; Wilson et al., 1987; Kyser and Kerrich, 1990; Kotzer and Kyser, 1991, 1995; Alexandre et al., 2005, 2009b). Up to now, the last hypothesis has prevailed.

The present results clearly show the presence of low δD brines. The unusually low δD values of brines require the involvement of a low δD component. A good candidate for low δD component is H₂ which was detected in variable amounts in fluid inclusions from McArthur River deposits by Derome et al. (2003a, 2005) and mineralized areas from Australian unconformity-related U deposits (Derome et al., 2003b). In these studies H₂ was sometimes associated to O₂ within fluid inclusions and was interpreted as resulting from water radiolysis. Water radiolysis is a common phenomenon in the environment of U deposits (Dubessy et al., 1988; Savary and Pagel, 1997). H₂ produced by water radi-

olysis has δD of $\sim -500\text{‰}$ (Lin et al., 2005). According to Dubessy et al. (1988), water radiolysis could either occur in any fluid in contact with U minerals, or within fluid inclusions having U-bearing daughter phase or dissolved U. Another possibility, compatible with statements from Dubessy et al. (1988), is that water radiolysis occurred within the mineralizing brines due to their high U content (Richard et al., 2010, 2012). In the latter case, dissolved and possibly molecular H_2 could have been present in the brines prior to the first stages of U deposition and could have acted as a reductant for U(VI).

Solid bitumens are widespread in the environment of unconformity-related U deposits (Landais and Dereppe, 1985; Leventhal et al., 1987; Landais et al., 1990, 1993; Landais, 1996; McCready et al., 1999; Alexandre and Kyser, 2006; McCready et al., 2007; Wilson et al., 2007). Petrographic analyses show that they formed during the late-stage. Based on $\delta^{13}C$ measurements on graphite and bitumen, Kyser et al. (1989) concluded that graphite was a possible precursor for bitumen. Using ion microprobe $\delta^{13}C$ measurements on bitumen, Sang  ly et al. (2007) proposed that CO_2 , originating from brine–graphite interaction, was combined with radiolytic H_2 to form hydrocarbons through Fischer–Tropsch-like reactions such as illustrated in the following equations:



Such reaction can produce low δD H_2O from low δD H_2 , although the δD value of H_2O produced is difficult to estimate due to uncertainties in hydrogen isotopic fractionation between hydrocarbons and H_2O . If the δD value of water produced by these reactions is similar to that of radiolytic H_2 ($\sim -500\text{‰}$), only a 10% mixing could account for a δD shift of brines from -50‰ to $\sim -95\text{‰}$. On the other hand, the residual water after radiolysis would acquire high δD values. This is hardly evidenced probably because radiolysis does not produce sufficiently high amount of low δD H_2 , and associated high δD H_2O . This raises the question of mass balance consideration on the volume of low δD water produced by combination of water radiolysis and Fischer–Tropsch-like reaction. Although this volume was probably small, discrete and incomplete mixing between brines and low δD water could account for not only for the low δD values of the mineralizing brines but also for (i) a minor part of the observed variability in fluid inclusion salinity and (ii) the heterogeneity of measured δD from one sample to another and even at the scale of individual quartz or dolomite veins, as previously shown by Pag  l et al. (1980).

Finally, the present results show that the low δD values of the mineralizing brines is one possible explanation to the low δD values of alteration minerals. Late re-equilibration with low temperature meteoric waters and radiation-catalyzed hydrogen exchange are not incompatible with the involvement of low δD brines but their relative importance for explaining low δD values of alteration minerals has to be re-evaluated.

6. CONCLUSION

The present study of quartz–dolomite veins and their fluid inclusions associated with unconformity-related U ores documents the evolution of evaporated seawater towards U-mineralizing brines.

Stable isotopes (O, H, C), radiogenic isotopes (Sr, Nd) and trace elements (including REE) bring new insights into (i) the temperature variation during hydrothermal events associated with high-grade alteration and UO_2 deposition, (ii) genetic links between quartz–dolomite veins, alteration minerals (illite, chlorite and dravite) and UO_2 , (iii) the extent of equilibration between brines host rocks, (iv) the consequence of brine–graphite interaction in the basement and water radiolysis for generating CO_2 and H_2 respectively, (v) the implication of Fischer–Tropsch-like reactions and abiogenic bitumen synthesis involving CO_2 and H_2 for generating anomalously low δD brines, (vi) the origin of the low δD values of alteration minerals around U ores.

The main findings are that the alteration minerals, quartz–dolomite veins and UO_2 have been equilibrated with similar brines in a progressively cooling system (~ 180 to $\sim 120^\circ C$). The brine composition has been drastically shifted from the original one (evaporated seawater) through extensive fluid–rock interactions, a key factor for efficient U mobilization in the Athabasca system.

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