

A detailed fluid inclusion study in silicified breccias from the Kombolgie sandstones (Northern Territory, Australia): inferences for the genesis of middle-Proterozoic unconformity-type uranium deposits

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Received 15 December 2001; received in revised form 30 July 2002; accepted 31 October 2002

Abstract

The relative chronology and detailed chemistry of paleofluids circulating at the base of the Kombolgie Sub-basin were investigated in the East Alligator River district (Northern Territory, Australia), where world-class unconformity-type uranium deposits are located. The chemistry of fluid inclusions was determined using in-situ analysis (Raman microprobe and laser-induced breakdown spectroscopy [LIBS]) and by observing the melting sequences by microthermometry. This study revealed the occurrence of three distinct fluids: (i) a sodium-rich brine that corresponds to a diagenetic fluid percolating at the bottom of the Kombolgie sandstones at a temperature close to 150 ± 15 °C; (ii) a calcium-rich brine, probably corresponding to a residual brine in evaporitic environment that has evolved by fluid–rock interactions with the basement lithologies; and (iii) a low salinity fluid, heated in the basement, injected into the base of the sandstone cover. H₂ and O₂ and/or traces of CH₄ were detected in the vapor phase of some fluid inclusions, especially in the low salinity ones in quartz breccia samples taken above mineralized areas. Hydraulic brecciation of the sandstone was associated with a pressure decrease favoring fluid mixing and the subsequent cementation of breccias. According to the fluid inclusion study and other geologic constrains, the minimum thickness of the Sub-Kombolgie Basin is estimated at 4 km. Drusy quartz breccias with evidence of fluid mixing are quite common at the base of the Kombolgie Basin, but not necessarily linked to U-mineralization. However, it is proposed that the presence of gases such as H₂ and O₂ in fluid inclusions, which results from water radiolysis, constitutes an indicator of gas linked to significant U concentrations deeper in the basement rocks.

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Keywords: Uranium; Fluid inclusions; Brines; Breccias; Unconformity; Radiolysis

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1. Introduction

The East Alligator River Uranium Field (McArthur Basin, Northern Territory, Australia) hosts major world-class unconformity-type uranium deposits, similar to the Athabasca Basin (Saskatchewan, Canada). Such deposits occur close to the unconformity (U/C) between a middle Proterozoic sandstone cover and an Archean to Lower Proterozoic metamorphic basement. Genetic models for both Australian and Canadian U-deposits invoke large-scale circulation of brines and their mixing with reducing fluid to explain uranium deposition (Wilde et al., 1989; Ypma and Fuzikawa, 1980) for Australian deposits (Hoeve and Sibbald, 1978; Hoeve and Quirt, 1987; Pagel et al., 1980; Fayek and Kyser, 1997; Kyser et al., 2000) and for Canadian ones. In the East Alligator River Uranium Field (EARUF), previous fluid inclusion studies were performed on basement rock samples from Nabarlek, Jabiluka (Ypma and Fuzikawa, 1980) and Koongarra (Wilde et al., 1989). A study of fluid inclusions in the sandstones overlying the Jabiluka deposit was investigated by Durak et al. (1983). Data from the literature are summarized in Table 1. They are somewhat difficult to fully integrate in a genetic model because they do not always provide the necessary information regarding: (i) detailed fluid chemistry at the scale of single fluid inclusions (wide range of salinities), (ii) relative chronology between highly saline and less saline fluids, (iii) microthermometric data ($T_{m_{ice}}/Th$ pairs, determination of the chemical system), and (iv) discrimination between the fluids related to ore deposition and those which may be related to early metamorphic events affecting the basement rocks.

Thus, to avoid confusion between retrograde metamorphic fluids and basinal fluids when studying basement rocks, the present fluid inclusion study mainly focussed on the paleofluids trapped in the sandstone formation. Moreover, the study was undertaken in both barren and mineralized areas in an attempt to distinguish parameters that lead to the uranium mineralization from the parameters that correspond to the bulk fluid regime at the base of the Kombolgie Sub-basin. The final aim of the present work is to propose a prospecting tool for this kind of uranium deposits.

The relative chronology between different fluid-types related to sandstone diagenesis and to breccia

cementation occurring both in the sedimentary cover and basement was first investigated. The precise observation of melting sequences in fluid inclusions and in-situ analytical techniques (Raman microprobe and laser-induced breakdown spectroscopy [LIBS]) were used to distinguish and characterize the different fluid-types. A reconstruction of the P , T , X evolution of the fluids is proposed and compared with data from the literature to improve the previous genetic models for Australian unconformity-type uranium deposits.

2. Geological setting

In the EARUF, the basement rocks consist of Archean and Early Proterozoic granito-gneisses of the Nanambu Complex, overlaid by the Kakadu Group gneisses and quartzites, and then by the metasediments of the epicontinental Cahill Formation. All these rocks underwent metamorphism during the Barramundi and Top End orogenies between 1870 and 1800 Ma (Needham, 1988). Metamorphism reached granulite facies conditions in the Nimbuwah Complex, east of the ARUF (Ferguson, 1980). A thick (up to 1500–1800 m presently preserved) unmetamorphosed detrital sequence composed of clastic sediments (the “Kombolgie Sub-group”) unconformably overlies the crystalline and metamorphic basement. The Kombolgie Sub-group consists of at least three sandstone units and conglomerate separated by volcanic units. Conglomerate beds, whose permeability may have played an important role in the circulation of fluids, are more common in the lower unit (the Mamadawerre Sandstone), which was deposited in a fluvial, high-energy environment. The intermediate unit (the Gumarrirribang Sandstone), which mainly consists of medium grained quartz arenites was deposited in a lower energy fluvial environment. The overlying well-sorted medium grained arenite corresponds to aeolian dune deposition conditions (Kyser et al., 2000). The youngest members of the Kombolgie Sub-group were deposited in marine conditions, as suggested by the occurrence of glauconite and halite crystal casts (Kyser et al., 2000), and of stromatolitic and evaporitic dolostone–sandstone in the McKay Formation (southeastern part of the McArthur Basin; Rawlings, 1999).

Two basaltic units are interlayered within the sandstones: the Nunbalgarri volcanics, located between the

Table 1
Summary of the previous fluid inclusion data obtained in the vicinity of the major deposits

Fluid inclusion type	Samples	FI type	trapped solids (EDAX)	Te (°C)	Tm _{ice} (°C)	TsNaCl (°C)	Th _L (°C)	Composition	Gases	Author
1	quartz vein close to mineralization	L + V _{10%} ± NaCl		nm	– 60 to 0	nm	~ 150	0–30% eq. CaCl ₂	CH ₄	(1)
	quartz in altered basement rocks	L + V _{10%}		– 45 to – 20	nm		150–175	0–10% eq. CaCl ₂	CO ₂	(3)
	detrital quartz grain boundary	L + V _{10%}			– 12.9 to – 6.3		125–215	9.3–16.8% eq. NaCl	No gas	(2)
	quartz overgrowth in sandstones	L + V _{10%}	hematite	down to – 70.4	– 44.9 to – 7.7		90–202	nm	No gas	(2)
2 (associated with type 1)	quartz vein	L + V _(10–90%)			nm			low salinity	CO ₂ and CH ₄	(1)
	quartz in altered basement rocks	vapor rich			nm		up to 400		CO ₂ + minor CH ₄ + N ₂	(3)
3	quartz vein-close to mineralization	L + V _{10%} ± NaCl			– 60 to 0	nm	~ 110	0–30% eq. CaCl ₂	CH ₄	(1)
	quartz less than 500 m away from mineralization	L + V + NaCl		– 60 to – 15	nm	110–236	125–150	20–45% eq. CaCl ₂	No gas	(3)
4		L + V + NaCl		nm	nm	114–185	66–147	nm	No gas	(2)
	quartz veins	L + V + NaCl	chl + wt + mica + daws + ht + goeth + carb + pitch	nm	nm		140–160	nm		(1)
	quartz veins and dolomites	L + V + NaCl	Fe-chl + white mica + carb + ht + apatite + kaol	nm	nm	125–242	< 125	30–45% eq. CaCl ₂	33 to 55 mol% CH ₄ + N ₂	(3)
	quartz veins	L + V + NaCl	Unidentified-occasionnal	down to – 70.4	< – 20.8	>220	91–148	nm		(2)

(1) Ypma and Fuzikawa (1980), (2) Wilde et al. (1989), (3) Durak et al. (1983). nm = not mentioned in the papers.

Mamadawerre and the Gumarrirrbang Sandstones, and the Gilruth volcanics overlying the Gumarrirrbang Sandstone. Both volcanic units caused contact metamorphism in the five upper centimeters of the underlying sandstones (Needham, 1988). Laterites, which occur at the base of these units and the basalt themselves, are enriched in U (Needham, 1988). The Oenpelli Dolerite sill locally reaches a thickness of several hundred meters and crosscuts the Kombolgie sandstones in the vicinity of the unconformity all over the ARUF. It was dated at 1720 Ma by $^{40}\text{Ar}/^{39}\text{Ar}$ (Deckart et al., submitted for publication). The Plum Tree Creek volcanics are unconformably overlaid by the Kombolgie subgroup. They were dated at 1822 Ma by U–Pb method using zircons (Page, 1994). According to these two limits, the deposition of the Kombolgie Subgroup is bracketed between 1822 and 1720 Ma (Sweet et al., 1999).

All uranium deposits in the ARUF, except for Nabarlek, are located in the Lower Cahill Formation. The dominant host lithologies for the ore are graphite, muscovite or feldspar quartz-schists, massive chlorite rock and chert frequently interbedded with marble (Needham, 1988). The oldest age for uranium deposition was estimated using U–Pb dating on whole rock samples at 1737 ± 20 Ma for the Ranger deposit (Ludwig et al., 1987). Jabiluka, Nabarlek, and Koon-garra deposits have been dated between 1600 and 1650 Ma using Sm–Nd and Rb–Sr methods on uraninites (Maas, 1989).

3. Sampling and petrography of samples

3.1. Sampling

Most of the samples studied in this work were taken from quartz breccia zones in the basal Kombolgie sandstones and in the basement rocks. The samples were selected over a 50-km long northeast–southwest profile (Fig. 1) including (i) Anomaly U65 (no U-mineralization), about 10 km south of the Nabarlek deposit; (ii) North Caramal area (no mineralization); (iii) Caramal U-showing (weakly mineralized area); (iv) South Horn area (weakly mineralized area); (v) Jabiluka U-deposit, about 50 km west from South Horn; and (vi) Ranger 3 U-deposit, about 20 km south from Jabiluka.

Several quartz generations were distinguished in sandstone samples and a general succession of quartz deposition was established (Fig. 2):

Q1: diagenetic epitaxial quartz overgrowths on detrital quartz grain that correspond to the first step of the sandstone cementation.

Q2: quartz filling intergranular voids that correspond to pervasive silicification representative of a later step of cementation.

Q3: millimeters to several centimeters long drusy quartz crystals cementing breccia bodies cross-cutting the sandstones that correspond to the third step of sandstone silicification, linked to a fracturation event.

Q4: euhedral amethyst quartz growing on Q3 that represents the latest silicification event observed in the studied samples.

3.2. Petrography of samples

Two samples from the Anomaly U-65 were studied: a well sorted sandstone, with Q1, Q3, and Q4. Hematite lamellae occur between the detrital quartz grains and their overgrowth (Q1). Rare idiomorphic titanium oxides, detrital tourmalines, and zircons occur in the authigenic siliceous cement. This sample is located 66.4 m above the unconformity. The second sample is an amethyst drusy quartz (Q4) taken about 123 m above U/C. Two clear drusy quartz veins (Q3) from North Caramal were taken in outcrop at 20–30 m above the unconformity. They contain hematite and goethite inclusions in the youngest growth lines. Six samples were taken in the vicinity of the Caramal uranium showing. Two representative lithologies from the basement were selected: a meta-arkose of the Cahill Formation crosscut by a hematized drusy quartz vein (43.75 m below U/C), and a gneiss of the Kakadu Group crosscut by a white quartz vein (21 m below U/C). These veins are undeformed and thus have clearly crystallized after the last metamorphic event, but their chronological relations with the quartz generations occurring in the sandstones cannot be determined from textural relations.

In the sandstones from the Caramal area, breccia bodies are from 10 to 100 m long and are up to 2–3 m thick (Fig. 3). Four pink to red fine-grained stratified sandstones samples were taken in different

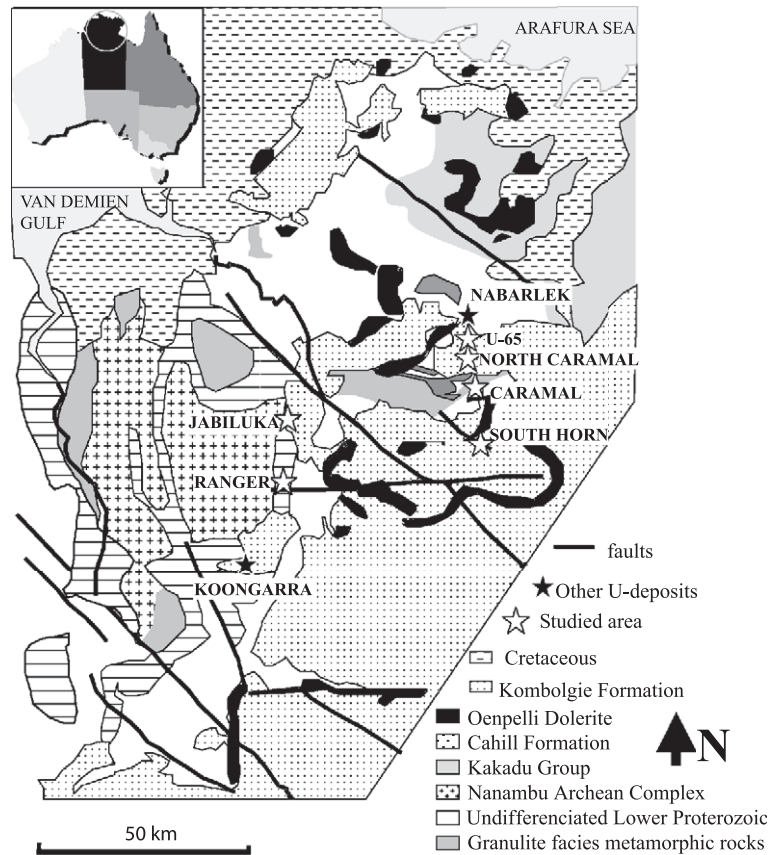


Fig. 1. Schematic geological map of the Alligator River Uranium Field, Northern Territory, Australia.

drill cores at 1–20 m from the U/C and 30–100 m from mineralization, in the vicinity of the breccias. This sampling covers the four silicification events

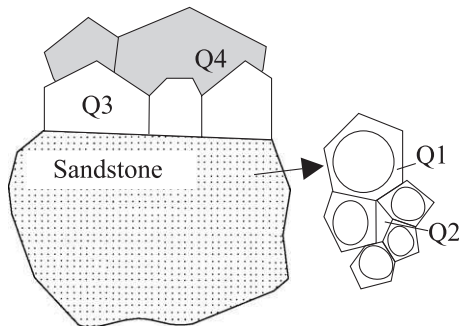


Fig. 2. Schematic representation of the relationships among the different types of quartz. Q1=diagenetic quartz overgrowth, Q2=quartz filling intergranular voids, Q3=drusy quartz cementing breccia and Q4=late quartz.



Fig. 3. "Vein-type" hydraulic breccia crosscutting the Kombolgie sandstone and cemented by drusy quartz. North-Caramal Area.

presented above (Q1, Q2, Q3, and Q4; Table 2). The sample from the South Horn prospect consists of white to limpid drusy quartz (Q3) crosscutting the highly chloritized Oenpelli Dolerite. Its distance to U/C is not known as the entire core was drilled in the dolerite. The closest U-anomaly occurs in the dolerite at about 150 m to the southwest of the drill core location. Three samples from the Jabiluka U-deposit were taken at less than 50 m from the ore zone. The two sandstones are pink-colored due to hematite lamellae trapped between detrital quartz and Q1. Both samples are slightly brecciated and cemented by Q3. The sandstone contains some detrital Ti-oxides and muscovites. One sample was taken from the basement. It consists of a metamorphic quartz vein in the foliation of a chloritized and weakly mineralized schist of the Cahill Formation (Fig. 4). Alteration products of U minerals occur at the walls of the quartz vein. Only the late fluid inclusion planes (FIP) were studied to minimize possible confusion with fluids related to metamorphism. One sandstone sample was taken from the Ranger 3 open pit, 10–20 m above the unconformity and about 20–50 m above the main ore zone. This sandstone is orange, medium-grained. It is

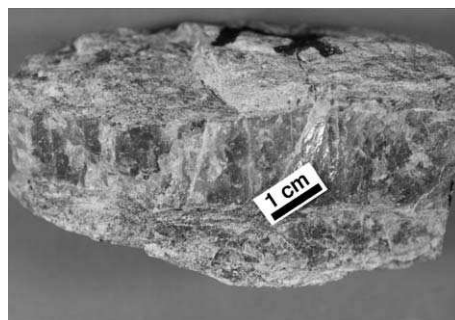


Fig. 4. Mineralized sample from the Cahill Formation, Jabiluka decline.

cemented by quartz (Q1) and brown-red to limpid chlorites. Hematite lamellae occur at the boundary between the detrital quartz and the quartz overgrowth. Brown to green detrital tourmalines occur in the cement of the sandstone. The sandstone is crosscut by a quartz vein (Q3). Dravite needles occur at the wall of Q3. The latter shows goethite and hematite inclusions in the latest growth lines. A summary of the characteristics of each sample is presented in Table 2.

Table 2

Summary of the studied samples and their distance to unconformity and mineralization

Location	Sample no.	Type	Drill hole-depth	Dist. to U/C	Distance to mineralization	Quartz generations
Ano U-65	NAB 02	Amethyst crystal	U65-2 surface	123 m		Q4
	NAB 03	Sst + qz breccia + amethyst	U65-2 54.20 m	66.4 m		Q1 – Q3 – Q4
North Caramal	NCA 02	Dsy quartz	outcrop	20–30 m		Q3
	NCA 03	Dsy quartz	outcrop	20–30 m		Q3
Caramal	33-CA-38	Sst + qz vein	CA38 41.8 m	10.5 m	73 m	Q1 + Q2 + Q4
	34-CA-43	Sst + dsy qz	CA43 45.8 m	14.35 m	~ 30 m	Q1 + Q2
	35-CA-45	Sst + dsy qz	CA45 46.3 m	19.3 m	~ 45 m	Q1 + Q2 + Q4
	36-CA-46	Sst + dsy qz	CA46 54.7 m	1.3 m	~ 90.55 m (from Th anomaly)	Q1 + Q2
	32-CA-30	Qz breccia in meta arkose	CA30 97.75 m	– 43.75 m		
	37-CA-38	Qz breccia in gneiss	CA38 212.95 m	– 20.95 m	– 97.5 m	
	CA 00 1	Drusy quartz breccia	outcrop	~ 20 m	~ 50 m	Q3
South Horn	97 SH 03	Drusy quartz breccia – Oenpelli dolerite	SHD001 105.4 m	^a	< 100 m	Q3
Jabiluka	8980-2	Sst + small dsy qz	decline	< 10 m	50 m (maximum)	Q1 + Q3
	8980-3b	Sst + small dsy qz	decline	< 10 m	50 m (maximum)	Q1 + Q3
	8979-7	Quartz vein in mineralized micaschist	decline	– 20–25 m	In the ore zone	Metamorphic quartz
Ranger 3 open-pit	RAN 3-4	Sst + dsy qz vein.	Open pit	Max. 10–20 m	20–50 m	Q1 + Q3

Sst = sandstone, Dsy = drusy quartz, Qz = quartz, Q1 = quartz overgrowth, Q2 = pervasive silicification, Q3 = drusy quartz breccia, Q4 = late quartz.

^a U/C not reached in this drill core.

4. Analytical techniques and methodology

Petrographic characteristics and relative chronology of fluid inclusions were studied for each quartz generation under an optical microscope. Low temperature microthermometry was performed on a Chaix-Meca cooling stage (Poty et al., 1976), using an Olympus optical microscope (objective 80 $\times$), to measure the eutectic, ice, and hydrate melting temperatures (respectively T_e , $T_{m_{ice}}$, and $T_{m_{hyd}}$). According to the calibration curves, ice and hydrate melting temperatures are given with an error of about ± 1 °C, whereas the errors on the first melting temperatures may have reached ± 5 °C and more for small fluid inclusions (<5 μ m) because of the difficulty observing the exact eutectic melting. Hydrates were identified using a LABRAM-DILOR Raman microprobe during cooling (Dubessy et al., 1982). Ice and hydrate melting temperatures obtained on the same fluid inclusions were used with the appropriate phase diagrams (Yanatieva, 1946) to determine composition of the aqueous phase. When hydrates were not observed, the Raman microprobe was used to determine the fluid chlorinity (Mernagh and Wilde, 1989). Homogenization temperatures (T_h) were measured using a USGS cooling–heating stage. The error on high temperature measurements was about ± 1 °C.

The Raman microprobe was also used to identify and quantify gases in the vapor phase of fluid inclusions (Dubessy et al., 1989). When all non-destructive analyses were performed, laser-induced breakdown spectroscopy (Dilor-NdYAG-UV266 nm) tests were done on fluid inclusions devoid of any solids to determine the cationic ratios of the liquid phase of fluid inclusions representative of each population distinguished by microthermometry (Fabre et al., 1999).

5. Results

5.1. Fluid inclusion petrography and microthermometry

Most fluid inclusions consist of a liquid phase and a small vapor bubble (~ 10 vol.%) at room temperature. Some contain trapped solids such as hematite, kaolinite or other unidentified solids.

Fluid inclusions in quartz overgrowth (Q1) are frequently small, indented or oval and do not contain any solid inclusions. $T_{m_{ice}}$ values are bimodal: -9.9 to -31.3 °C and -38.5 to -45 °C (Fig. 5a). The latter group was found only in the Ranger 3 open-pit sandstone, where the fluid is trapped along FIP crosscutting the quartz overgrowths and thus is secondary with respect to the early diagenesis. Eutectic melting could not be observed because of the small size of the inclusions. Homogenization always occurs in the liquid phase between 100 and 181 °C, with a maximum frequency around 135 °C, for primary fluid inclusions and between 89 and 120 °C, with a maximum frequency around 110 °C for secondary fluid inclusions (Fig. 5f).

Fluid inclusions in late silicifications (Q2) are small (<15 μ m) and oval. They do not contain any solid inclusions. Their microthermometric characteristics are quite similar to the inclusions from Q1, except that fluid inclusions with low $T_{m_{ice}}$ are not secondary. T_e values range from -67.5 to -35 °C, $T_{m_{ice}}$ varies from -49.4 to -13.1 °C, and T_h varies from 100 to 177.5 °C (Fig. 5b) with the majority of data between 120 and 150 °C (Fig. 5f).

Primary fluid inclusions in drusy quartz (Q3) have much larger sizes than the preceding ones (20–60 μ m). They often possess an irregular or rectangular shape, with their elongation oriented perpendicular to the growth zones of the drusy quartz. They frequently contain solid inclusions such as hematite or kaolinite (identified from their Raman microprobe spectra) and/or other unidentified white to green solid phases occurring as stacked sheets that probably correspond to chlorites. The occurrence of such solids will not be discussed further since it corresponds to heterogeneous trapping and since these solids could not be attributed to a fluid type. These fluid inclusions are characterized by very low T_e values ranging between -65 and -45 °C, but some values are close to -25 °C, a wide range of $T_{m_{ice}}$ (-51.7 and -0.02 °C) and T_h (87–210 °C with a maximum frequency between 100 and 140 °C) (Fig. 5c and f). Some fluid inclusions present yellowish hexagonal crystals that persist after the melting of ice (in this case, it is close to -25 ± 2 °C), up to $+8.6$ °C. This solid was identified as hydrohalite by Raman microprobe. Careful observations show that fluid inclusions with the highest $T_{m_{ice}}$ and those with low $T_{m_{ice}}$ were both

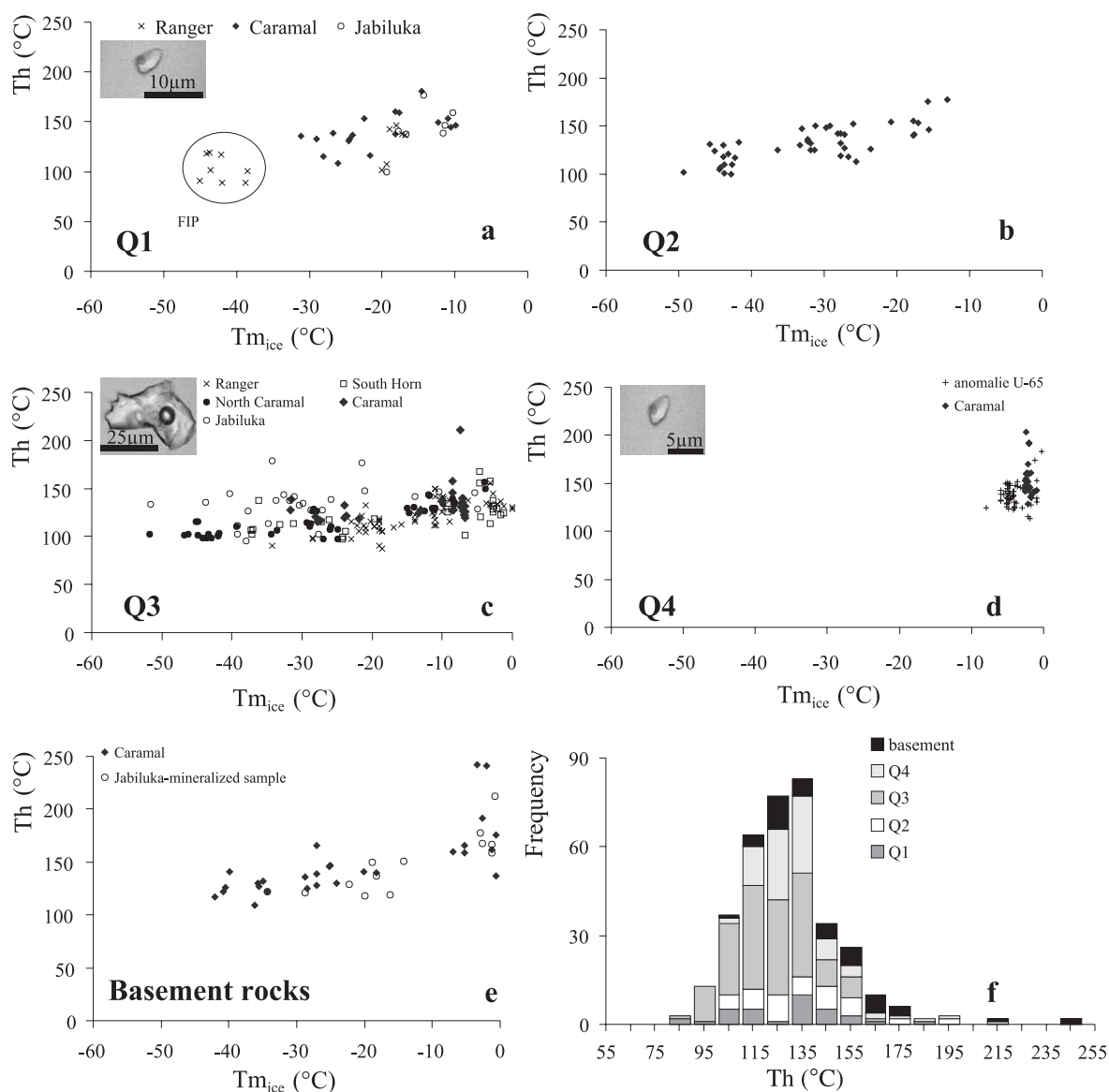


Fig. 5. (a)–(e) Tm_{ice}/Th diagrams obtained in each type of quartz. FIP=fluid inclusion plane. (a) Quartz overgrowth (Q1), (b) quartz filling intergranular voids (Q2), (c) drusy quartz cementing breccia (Q3), (d) quartz veinlets and amethyst quartz (Q4), (e) quartz veins from the basement, (f) frequency histogram of Th for each type of quartz.

observed within the same growth zones, whereas late fluid inclusion planes contains only fluid inclusions with high Tm_{ice} and eutectic temperatures close to –25 °C.

Fluid inclusions located in the latest quartz (Q4) are often 15–25 μm in size and frequently shaped as negative crystals. Fluid inclusions have high Te (–35

to –24 °C) and Tm_{ice} (–7.9 to 0.3 °C), with a large range of Th (113–201.3 °C), most of them ranging from 120 to 160 °C (Fig. 5d and f).

Fluid inclusions from quartz veins in the basement rocks from Jabiluka and Caramal are frequently <20 μm. Their microthermometric characteristics also vary largely as in Q3 (–70 < Te < –40 °C, –42 <

$T_{m_{ice}} < -0.6$ °C, $109 < Th < 240$ °C, with a maximum of data comprised between 120 and 180 °C; Fig. 5e and f).

All data are summarized in Table 3. The whole set of ice melting temperatures from the different quartz generations is represented in a frequency histogram (Fig. 6a), which shows three modes $T_{m_{ice}}$: around -42.5 °C, around -25 °C, and around -2.5 °C. Homogenization temperatures corresponding to the three groups are also presented in a histogram (Fig. 6b) that clearly shows that the fluid inclusions with the lowest $T_{m_{ice}}$ also have the lowest Th and conversely.

5.2. Fluid compositions

Since eutectic temperatures of fluid inclusions were frequently below the T_e of the H_2O – $NaCl$ system, it was necessary to determine the detailed composition of individual fluid inclusions by techniques other than microthermometry. Chlorinity and cation ratios were determined by using Raman microprobe and LIBS on a couple of fluid inclusions covering the whole set of microthermometric characteristics (low, intermediate, and high $T_{m_{ice}}$, and also on fluid inclusions presenting hydrohalite as the last melting phase). These analyses were only performed on samples from South Horn, Caramal, North Caramal, and Ranger, in drusy quartz cementing breccias (Q3), where all fluid-types are represented (Fig. 5d) and where fluid inclusions are large enough for LIBS analyses (>20 μm) and devoid of solids.

The coupling of Raman (for chlorinity measurements and gas analyses) and LIBS (for cation ratios) has confirmed that three types of fluid exist, all

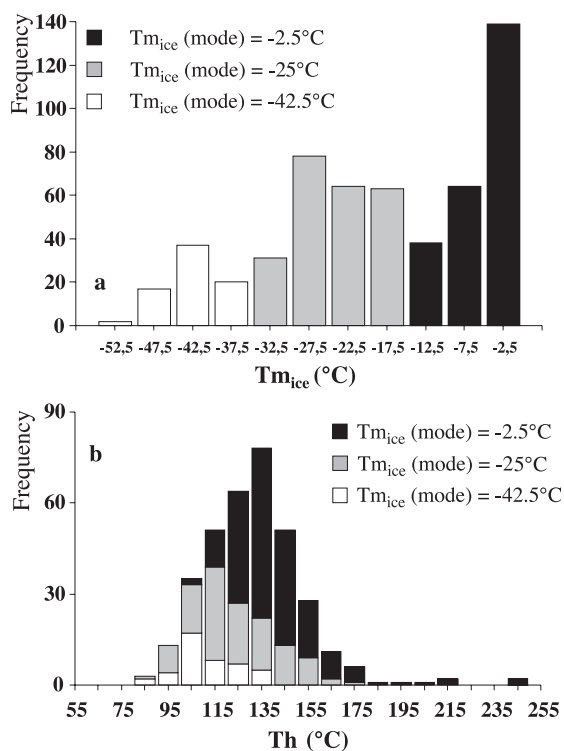


Fig. 6. (a) Histogram of ice melting temperatures measured in all samples showing three groups of $T_{m_{ice}}$, corresponding to three fluid types: below -35 °C, between -35 and -15 °C, and above -15 °C. (b) Histogram of homogenization temperatures for each type of fluid.

belonging to the H_2O – $NaCl$ – $CaCl_2$ system (Table 4), as already suspected from microthermometric studies.

Fluid inclusions with mean Th values of 105 °C and $T_{m_{ice}}$ below -35 °C have the highest chlorinity

Table 3

Microthermometric data of fluid inclusions located in the different types of quartz. T_e : eutectic temperature, $T_{m_{ice}}$: ice melting temperature, $T_{m_{hyd}}$: hydrohalite melting temperature, Th: homogenization temperature

Quartz	Shape	Size (μm)	Vapor phase (vol.%)	T_e (°C)	$T_{m_{ice}}$ (°C)	$T_{m_{hyd}}$ (°C)	Th (°C)	Solids
Q1	indented/oval	~ 5	12	n.o.	-31.3 to -9.9	n.o.	99.7–181	n.o.
Q2	oval, irregular or rectangular	<15 –50	10	-67.5 to -45	-49.4 to -13.1	n.o.	100–177.5	kaol $\pm$ hem $\pm$ phyll
Q3	irregular or rectangular	20–60	10	-65 to -48 ; -25^a	-51.7 to 0	-13.7 to $+8.6^a$	87–210.5	kaol $\pm$ hem $\pm$ phyll
Q4	negative crystal	15–20	10–15	-35 to -24	-7.9 to -0.3	n.o.	113–201.3	n.o.
Basement	irregular	<20	10–15	-70 to -40	-42 to -0.6	n.o.	109–240	phyll

^a Occasionally observed in fluid inclusions. n.o. = not observed, kaol = kaolinite, hem = hematite, phyll = phyllosilicates.

Table 4

Summary of the characteristics of the three fluid-types: microthermometric, LIBS (cation ratios) and Raman data (chlorinity and gases)

Fluid-type	T _{mice} (range) (°C)	Raman chlorinity (mol/kg H ₂ O)	Na/Ca (LIBS)	Th (range) (°C)	Gases (traces amounts)
Ca–Na brine	–42.5 (–35 to –51.7)	5.5 (5–6)	0.1 (0.07–1)	105 (89–144.5)	N ₂ , CO ₂ , CH ₄
Na–Ca brine	–25 (–15 to –35)	5 (4–6)	8.2 (2–8.5)	115 (87–179.1)	CH ₄ + N ₂ ; H ₂ ± O ₂
Low saline fluid	–2.5 (–15 to 0)	2.1 (4.3–0.75)	1–10.5	135 (101–242.4)	CH ₄ ± H ₂ ± O ₂

(around 5.5 mol/kg H₂O) and the lowest Na/Ca ratios (from 0.07 to 1). Thus, this high salinity fluid is Ca-dominated and is designated as Ca–Na brine. Traces of N₂, CO₂, and CH₄ (respective proportions in the vapor phase: 66%, 21%, and 13%) were detected by Raman microprobe in the vapor phase of some of the Ca–Na brine inclusions in Q3 from North Caramal.

Fluid inclusions with mean Th values of 115 °C and intermediate T_{mice} (mean value of –25 °C) correspond to the same fluid-type as those presenting hydrohalite as last melting phase (T_{mice} close to –25 °C and T_{mhydrohalite} up to +8.6 °C). Their chlorinity values are close to 5 mol/kg H₂O and Na/Ca ratios range from 2 to 8.5. This Na-dominated, saline fluid is thus designated as Na–Ca brine. Traces of CH₄ and N₂ (CH₄/CH₄ + N₂ from 0.2 to 1) were occasionally detected in the vapor phase of some Na–Ca brine inclusions in Q3 samples from all studied areas but mostly in samples from Ranger 3 and Caramal and Jabiluka.

Fluid inclusions with mean Th values of 135 °C and T_{mice} above –15 °C present the lowest chlorinity values (down to 0.75 mol/kg H₂O) and highly variable Na/Ca ratios (from 1 to 10.5). This fluid type corresponds to a hot and low salinity fluid. Significant amounts of H₂ and CH₄ (up to 30% H₂) were commonly associated with this fluid type in Q3 from Caramal uranium showing and Ranger 3 deposit. In the basement sample from the Jabiluka uranium deposit, H₂ and O₂ were frequently identified, with occasional traces of CH₄ and N₂. Such traces were also occasionally observed in barren zones, but without H₂ or O₂.

6. Discussion

6.1. Chronology of fluid circulation

The relative chronology between the three fluid-types described above was determined from the petro-

graphic and microthermometric study of fluid inclusions in the different quartz generations. The apparition of each fluid type is linked with a step of cementation of the sandstone (Table 5):

- (i) The first fluid trapped in quartz overgrowths (Q1) in the sandstone is interpreted as the early diagenetic fluid. Fluid inclusions in Q1 are too small to use LIBS and Raman analyses to determine the chemical composition of their aqueous phase. However, these techniques were used on fluid inclusions from Q2 and Q3, which show similar microthermometric characteristics as fluid inclusions trapped in Q1 (i.e. with T_{mice} around –25 °C). Raman and LIBS analyses have shown that fluid inclusions showing T_{mice} close to –25 °C correspond to the Na–Ca brine, either in Q1, Q2, or Q3. However, its bulk salinity increases progressively from Q1 to Q3 as shown by the apparition of hydrohalite as the last melting phase in some fluid inclusions from Q3.
- (ii) The Ca–Na brine occurs in healed microcracks in Q1. However, it appears together with the Na–Ca brine, in Q2, with no evidence of microcracks that would suggest that the Ca–Na brine was recorded in Q2 during a late fracturation event. This brine is also present in quartz cementing

Table 5

Summary of the different types of quartz and their correspondence with silicification events

	Quartz	Na-Ca fluid	Ca-Na fluid	Low salinity fluid
Early silicification	Q1	+ Salinity -		
Pervasive	Q2			
silicification				
Brecciation	Q3			
Final filling of fractures	Q4			

breccia (Q3). The simultaneous occurrence of Ca–Na and Na–Ca brine in Q2 and Q3 in the sandstones and in the basement rocks is confirmed by evidence of partial mixing between the two fluids (Fig. 5b, c, and e).

(iii) The low salinity fluid starts to appear in the drusy quartz cementing the hydraulic breccias (Q3) together with both Na–Ca and Ca–Na brines, and is finally predominant in Q4. Mixing evidences of the low salinity fluid with the brines attest that the three fluid types have circulated together and were trapped at the same time, e.g. during the cementation of breccias.

6.2. Trapping conditions

The isochores of the two brines (Na–Ca and Ca–Na) were calculated by the equation of state of Zhang and Frantz (1987) using their microthermometric characteristics presented in Table 4. The mean isochores of each brine were plotted in a P – T diagram (black and gray lines in Fig. 7) together with isochores calculated with the lowest and highest Th (dotted lines). Lithostatic and hydrostatic geothermal gradients of 25 and 35 °C/km were plotted in the same diagram. These thermal gradient values are in agreement with the 35 °C estimated by Pagel et al. (1980) in the Athabasca Basin and with the 28 °C/km that corresponds to the mean geothermal gradient for normal continental basins (Robert, 1985).

As the lower part of the Kombolgie sandstone in this area is frequently strongly silicified and presents horizontal stylolites due to severe compaction of the sedimentary pile, it can be assumed that the two brines were trapped under lithostatic pressure conditions during burial of the sandstones. The minimal isochore of brines intersect the lithostatic geothermal gradients of 30 ± 5 °C/km at a pressure close to 1125 ± 250 bars corresponding to a depth of about 4.5 ± 1 km and a temperature of 150 ± 20 °C. These P – T estimates correspond to the minimal conditions prevailing during sandstone burial.

A depth estimation of 4.5 km implies a minimal denudation of about 2 km of sedimentary cover since diagenesis. This interpretation is at variance with that of Wilde et al. (1989) who assumed that the present thickness of the Kombolgie sandstone in the EARUF (<2000 m) has not changed since the formation of

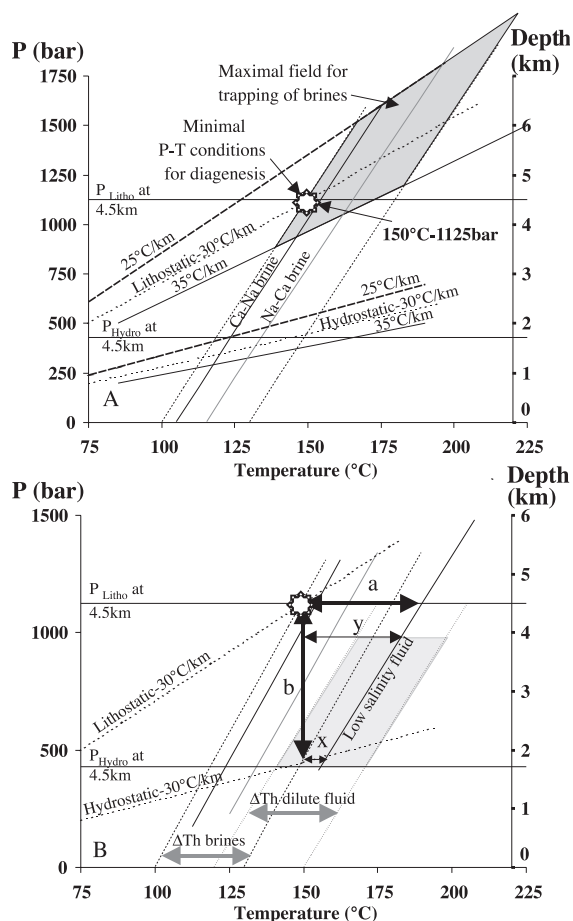


Fig. 7. P , T diagrams for fluids occurring in the Kombolgie Subgroup. (A) Trapping conditions of the brines at the base of the Kombolgie Sub-basin during diagenesis. (B) Mixing conditions: (a) anisothermal mixing at $4.5 (\pm 0.5)$ km under lithostatic pressure; (b) isothermal mixing under pressure changes.

unconformity-type uranium deposits. Such an assumption yielded to an abnormally high geothermal gradient of 100 °C/km, which is far from what can be expected in an intracratonic sandstone sedimentary basin.

The isochore of the low salinity fluid (Fig. 7b) intersects the geothermal gradient of 30 ± 5 °C/km at pressures of about 1.700 ± 500 bars, which would correspond to a thickness of the sandstone cover of about 7 km. However, the low salinity fluid was mixed with the two brines during brecciation and trapped together within growth zones of drusy quartz cementing breccias. Thus, the low salinity was trapped under the same pressure conditions as the

brines, e.g. about 1125 ± 250 bars. Therefore, two different mixing conditions have to be discussed to explain the simultaneous occurrence of such different fluids at the scale of a quartz growth line.

6.2.1. Isobaric mixing

Brines and low salinity fluids were trapped under the same pressure conditions during diagenesis (arrow a, Fig. 7b). In this case, the mixing between brines (150 °C) and the low salinity fluid is anothermal, within about 40 °C. However, such a mixing seems to be impossible under strictly lithostatic pressure conditions.

6.2.2. Non-isobaric mixing

The two brines and the low salinity fluid were mixed and trapped at the favor of pressure decrease from lithostatic to hydrostatic regime (arrow b, Fig. 7b). This pressure decrease of about 750 bars covers the range of Th of the brines (ΔT_h brines in Fig. 7b), represented by their two extreme isochores rooted at 100 and 130 °C in the P – T diagram (Fig. 7b). In such extreme conditions of pressure decrease, the mixing could be interpreted as nearly isothermal.

Hydraulic brecciation, fluid mixing, and T_h variations are in agreement with a drastic pressure decrease that was probably induced by basement fault reactivation. However, a pressure decrease of 750 bars corresponds to the maximal possible pressure decrease, between lithostatic and hydrostatic pressure regimes. The drop of pressure was probably less important. Since no other constrains allow the determination of the exact pressure of entrapment, it is proposed that breccia formation and fluid mixing occurred between infralithostatic (about 1000 bars) and hydrostatic pressure regime (430 bars in the present case). Thus the temperature of the low salinity fluid was in between 160 and 180 °C (intersection of arrows x and y with the mean isochore of the low salinity fluid—Fig. 7b).

In summary, the P – T history of the basis of the Kombolgie Formation recorded in Q1, Q2, Q3, and Q4 can be summarized in two steps:

1. The Kombolgie sandstones were progressively buried and cemented by quartz (Q1 and Q2) under infralithostatic pressure regime. According to the P – T diagram (Fig. 7b) the thickness of the basin reached at least 4.5 km and the temperature at the

base of the basin can be estimated at ca. 150 ± 20 °C from brine inclusions and assuming a geothermal gradient of 30 ± 5 °C/km.

2. Fault reactivation induced a pressure decrease in the order of 750 bars. This pressure decrease allowed the circulation of brines at the base of the basin and their percolation in the basement rocks. This tectonic activity probably initiated the injection of the low salinity fluid at the base of the sandstones and their subsequent hydraulic brecciation. Breccias represent preferential pathways for fluid circulation, and thus an efficient mixing zone for the three fluid-types. The combined effect of temperature decrease of the low salinity fluid and salinity decrease of brines induced by their mixing is probably at the origin of the cementation of breccia (Walther and Helgeson, 1977) by drusy quartz (Q3 and Q4).

6.3. Origin of fluids

As it was previously discussed, the Na–Ca brine corresponds to the diagenetic fluid that circulated during the cementation of the Kombolgie sandstone. The occurrence of Ca–Na brine is less common in sedimentary basin. High Ca content may be partially explained by a relative Ca enrichment of the residual brine after halite precipitation (Hanor, 1994). This highly concentrated brine may represent formation waters of evaporitic origin. Evaporitic levels from which such brines should have been expelled are described in the McKay Formation where halite crystal casts were observed (Rawlings, 1999; Kyser et al., 2000). However, although this process can explain the calcium content of the Na–Ca diagenetic brine, it cannot explain Na/Ca ratio as low as 0.07 obtained on a couple of fluid inclusions from Q3. Therefore, the Ca–Na brine may result from the evolution of formation waters from evaporitic environment by circulating in the Ca-rich basement lithologies. Although these rocks are not strongly altered after metamorphism in non-mineralized areas, they are in the immediate vicinity of the deposits. Thus, calcium exchange between the Na–Ca brine and calcium-rich basement lithologies is probably the major process that lead to the genesis of the Ca–Na brine. Leaching of the Oenpelli dolerite could also have lead to a Ca enrichment of the diagenetic brine,

however fluid inclusion studies in the quartz breccia crosscutting the dolerite did not reveal a difference in the fluid composition with respect to samples taken far away from it. Thus, the chemical effect of the dolerite intrusion is probably limited.

The low salinity fluid is slightly warmer and presents more frequent and more significant occurrence of CH_4 than the brines. A reasonable assumption is to consider that this fluid has circulated through deep faults in the basement rocks, where it has been heated and where it has probably reacted with graphite to produce small amounts of CH_4 . The low salinity of this fluid suggests a probable meteoric origin. However, further studies, such as punctual isotopic analyses of host quartz, should be done to confirm the origins of the Ca–Na brine and the low salinity fluid.

6.4. Comparison with the fluids occurring in the vicinity of the main deposits (Jabiluka, Nabarlek, and Koongarra)

6.4.1. Fluid inclusion type and composition

The first fluid inclusions study in the EARUF was performed by Ypma and Fuzikawa (1980) in the basement rocks of the Nabarlek and Jabiluka deposits. The authors describe two distinct fluid inclusion types: vapor-rich medium to low salinity fluid inclusions with CO_2 and CH_4 in their vapor phase, and complex brine inclusions (containing CaCl_2 , MgCl_2 , NaCl , KCl , and FeCl_2) with numerous trapped solids. Their bulk salinity range from 0 to 30 eq. wt.% CaCl_2 . The small vapor phase of the latter inclusions may contain CH_4 .

Wilde et al. (1989) also studied fluid inclusions in the basement rocks at Nabarlek, Jabiluka and Koongarra. They described four types of fluids: early metamorphic fluids, pre-ore fluid with salinities ranging from 0 to 10 eq. wt.% CaCl_2 and traces of CO_2 , a syn-ore fluid with salinities ranging from 20 to 45 eq. wt.% CaCl_2 with no gas, and a post ore fluid that have salinities of 30–45 eq. wt.% CaCl_2 with $\text{CH}_4 + \text{N}_2$. This late brine is associated with halite cubes and numerous trapped solids in fluid inclusions.

The only fluid inclusion study performed in the sandstone was done by Durak et al. (1983) at Jabiluka. The authors distinguished four types of fluid inclusions: those trapped on the detrital grain boundary have salinities of 9.3–16.8% NaCl ; fluid inclusions in

quartz overgrowth have higher salinities as suggested by $T_{m_{ice}}$ down to -44.9°C and the presence of halite crystals in some fluid inclusions; and fluid inclusions trapped in quartz veins have the highest salinities according to their halite dissolution temperatures. No gases were detected in any fluid inclusion.

All these fluid inclusion data have been regrouped into four types according to their similarities (Table 1) and according to the comparison proposed by Wilde et al. (1989). Previous data will tentatively be compared to ours.

Type 1 fluid inclusions observed in the quartz overgrowths of the sandstones as well as in basement quartz present T_h and $T_{m_{ice}}$ values nearly encompassing the whole range of compositions observed in Q1, Q2, and Q3 from our study (Table 3). According to the present study, and since the authors do not distinguish several fluid flow events from crosscutting relationships, such a range of composition can be interpreted as the result of mixing of a hot and low salinity fluid with brines.

Type 2 fluid inclusions (vapor-rich in Table 1) were rarely observed in our samples. Their composition could not be determined because the liquid water film along the walls of the inclusions was too thin and did not allow the determination of $T_{m_{ice}}$ or T_h during microthermometric measurements. In the present work, Raman microprobe analyses of the large vapor phase did not reveal any gas in these fluid inclusions, contrary to the observations of Ypma and Fuzikawa (1980) and Wilde et al. (1989).

Type 3 fluid inclusions (Table 1), correspond to both NaCl and CaCl_2 dominated brines that were clearly distinguished in our study. However, type 3 inclusions containing a halite cube were rarely observed in our samples, indicating significantly higher salinity.

Type 4 solid-rich fluid inclusions (Table 1) also probably correspond to the two brines from the present work, as suggested by the range of salinities and temperatures. However, the range of halite dissolution temperature suggests higher salinities. These fluid inclusions also contain numerous heterogeneously trapped phyllosilicates that seem to be less frequent in the samples of the present study and in sandstone samples of Durak et al. (1983). This could be due to the fact that our sampling in the sandstones was performed in non- or weakly altered rocks, thus

heterogeneous trapping of alteration minerals was less frequent.

The present fluid inclusion study revealed for the first time the occurrence of two distinct brines at the base of the Kombolgie basin and the injection of a hot and low salinity fluid, which was responsible for the dilution of the brines. This fluid was contemporaneous with hydraulic breccia cementation by drusy quartz. Previous microthermometric studies suggests that this low salinity fluid was also present in Jabiluka, Nabarlek, and Koongarra, but its chronology and composition was not clearly distinguished from the other fluids.

6.4.2. Gases

Previous studies have shown the occurrence of CO₂ in types 1 and 2 and CH₄ and N₂ in types 2, 3, and 4 fluid inclusions from basement rocks (Table 1). However, the exact significance and origin of these gases were not established since they could also be linked to the metamorphic history of the basement. In the present study, methane most frequently occurs in the gas phase of the hot and low salinity fluid. The occurrence of reduced carbon species in this fluid may result from its greater ability to react with graphite in the basement because of its higher temperature compared to brines. Mixing of the hot and low salinity fluid with the brines would explain the presence of methane in some of the highly saline fluid inclusions. However, the presence of CH₄ in brines (mainly Na–Ca) due to organic matter degradation during diagenesis cannot be excluded.

CO₂ and N₂ have been observed in the Ca–Na brine, together with traces of CH₄. Such gases could attest of the highest oxidizing character of this brine with respect to the other fluids. H₂ associated or not with O₂ were only found in the mineralized areas (Caramal, Jabiluka and Ranger). The occurrence of H₂ may result from reactions of Fe-chlorite or pyrite with H₂S (Hedenquist et al., 1992) through Eqs. (1) and (2) presented below:



Since H₂S has not been observed in our samples nor in the previous studies, the most probable explanation for the presence of these gases in the vicinity of

U-deposits is water radiolysis (Kish and Cuney, 1981; Dubessy et al., 1988; Krylova et al., 2002). Oxygen, which is normally produced together with hydrogen during water radiolysis, may have been used in oxidation reactions before being trapped in the fluid inclusions that present only H₂. The simultaneous occurrence of hydrogen and oxygen and, to a lesser degree methane in the breccia zones of the Kombolgie sandstone, coupled with other geologic constraints may represent an interesting marker of the proximity of U-mineralization.

7. Fluid regime in the EARUF-consequences for uranium mineralization

7.1. Previous genetic models

Two distinct genetic models, mainly based on fluid inclusion studies, were previously proposed for Australian unconformity-type uranium deposits:

- (i) Ypma and Fuzikawa (1980) invoked the mixing between two fluids: a low salinity CO₂-rich oxidized fluid, transporting uranyl-complexes (type 2 fluid—Table 1), and a highly saline brine containing CH₄ (type 1 or 3). This mixing resulted in unmixing of a CO₂–CH₄ gas phase. The low pH of the highly saline brine would have induced the destabilization of the uranyl-complexes and CH₄ caused the reduction of the uranyl ions to form uraninite. Temperature of uranium deposition was estimated to be between 110 and 160 °C, at a pressure of about 300 bars, corresponding to burial depths comprised between 1200 and 3000 m according to the chosen pressure regime, i.e. lithostatic or hydrostatic.
- (ii) Wilde et al. (1989) proposed that the type 3 fluid (L + V + NaCl) represents the syn-ore fluid since it occurs exclusively at less than 500 m from the ore zones. The type 4 fluid would be a post ore fluid (Table 1), because solids belonging to the alteration paragenesis associated with the ore deposits were trapped within fluid inclusions. The reduction of uranium-bearing brine would be due to aromatic hydrocarbons whose origins are not discussed in the paper. CH₄ directly observed in the inclusions would result from the reaction

between those hydrocarbons and the brine. A temperature of uranium deposition of about 200 °C was estimated from fluid inclusion and fission track analyses on zircons. A maximum depth of 2000 m, resulting in an abnormally high geothermal gradient of 100 °C/km was assumed.

7.2. Model of fluid circulation in the EARUF-possible consequences for U-mineralization

A model of fluid circulation based on present and previous fluid inclusion studies in basement and sandstone cover is proposed (Fig. 8). The diagenetic Na–Ca brine circulates in thermal equilibrium with the sandstones (150 ± 20 °C) under infralithostatic pressure conditions at a minimal depth of ca. 4.5 km (Fig. 8-1). Due to its density (about 1.02), the Na–Ca brine infiltrates the basement rocks, where it is progressively enriched in Ca to form the Ca–Na brine. At the favor of fault reactivation, the Ca–Na brine is introduced at the base of the basin and trapped together with the Na–Ca brine in Q2 (Fig. 8-2). The occasional occurrence of CO₂ and N₂ in the vapor phase of fluid inclusions in relation to this brine could attest of the oxidizing potential of this Ca–Na brine. Previous and present fluid inclusions studies in the basement lithologies suggested that the Na–Ca and the Ca–Na brines circulated within the basement rocks where they could have released uranium from U-bearing minerals (Cuney and Mathieu, 2000). Then a pressure decrease probably induced by basement faults reactivation initiated hydraulic brecciation linked to the injection of the slightly hotter (170 ± 10 °C) low salinity fluid at the base of the impervious Kombolgie sandstone. The opening of breccias allowed the mixing between the brines and the low salinity fluid (Fig. 8-3). Above mineralized areas, these breccias have recorded these mixings and the upward migrations of gases such as H₂ and O₂ produced by water radiolysis at the contact of U-mineralization.

The oxidized brines represent the most probable vector of dissolved uranium, and especially the Ca–Na one due to its probable higher oxidizing potential and its lower pH due to its high salinity (Hanor, 1994). Up to now, methane or heavier hydrocarbons were considered as reducing agents responsible for the destabilization of uranyl complexes.

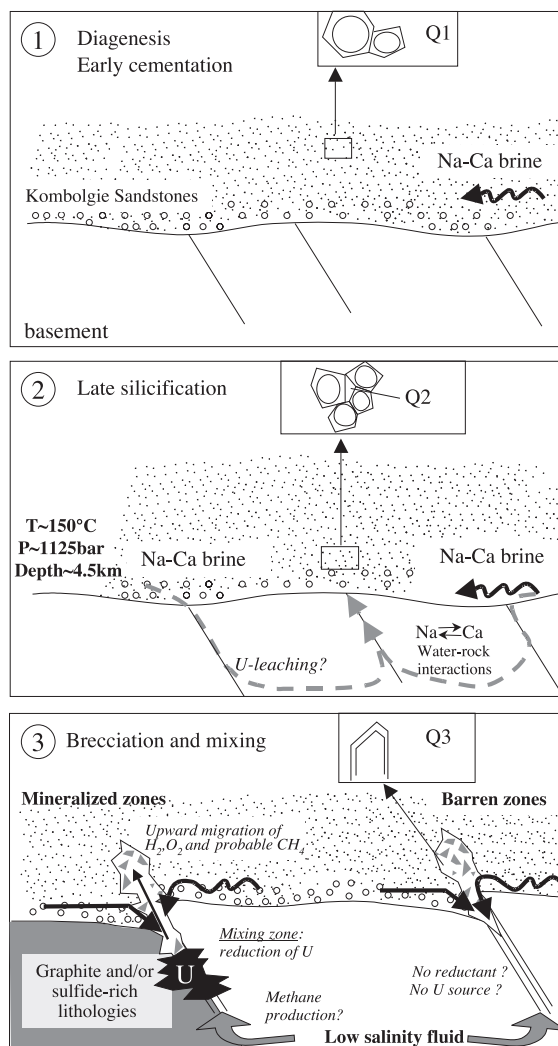


Fig. 8. Schematic sketches of fluid circulation at the base of the basin for each step of silicification event. Possible implications for the genesis of Australian unconformity-type uranium deposits.

An attempt to find oil inclusions was undertaken during the present study without any success. But upward circulation of low salinity fluids associated with traces of methane in relation with the reactivation of major basement faults was evidenced. These fractures represent the best candidates for a reaction between fluid and graphite from basement lithologies to produce at least small amounts of CH₄ that could represent the reducing agent needed for uranium deposition.

Thus the mixing of U-bearing brines with the hot and low salinity fluid associated with CH₄ could represent a part of the bulk process that enabled the uranium deposition. However, the reduction of uranyl complexes by divalent iron from basement lithologies as proposed by Komninou and Sverjensky (1996) probably represents an additional mechanism for the reduction of uranyl ions and may account for the bulk efficiency of uranium deposition. The occurrence of breccia is common in the EARUF and not necessarily linked to uranium deposits. Mixing between the three types of fluids were observed both in barren areas and in mineralized ones. A crucial parameter for U-deposition is lacking in barren zones. This could be the production of CH₄ that is less efficient or absent due to graphite-poor basement lithologies or a lack of potential U-sources in the environment.

8. Conclusions

- (i) Three types of fluids were identified in the Kombolgie sandstone: a low temperature diagenetic Na–Ca brine, a low temperature Ca–Na brine, and a hotter-low salinity fluid. The three end-members show evidence of mixing.
- (ii) The minimal temperature at the base of the Middle Proterozoic Kombolgie Sub-basin during the maximal burial stage was 150 ± 20 °C, assuming a geothermal gradient of 30 ± 5 °C.
- (iii) The Kombolgie Sub-basin has reached a thickness of at least 4.5 km, during the maximal burial stage at variance with the much lower previous estimates by Ypma and Fuzikawa (1980) and Wilde et al. (1989).
- (iv) Quartz cementation at the base of the Kombolgie Sub-basin occurred in two steps with an early diagenetic cementation synchronous with the Na–Ca brines and a later cementation corresponding to the onset of the Ca–Na brine circulation, which led to the filling of the residual porosity of the sandstone.
- (v) A hot and low salinity fluid was injected at the base of the basin as a result of basement fault reactivation and subsequent pressure decrease. Both fluid pressure and tectonic activity induced the formation of the hydraulic breccias commonly observed at the base of the Kombolgie sandstones. These breccias constitute preferential mixing zones for the three fluid-types.
- (vii) Breccia bodies seem to have recorded mixing probably linked to the ore-forming processes. They could be used as an efficient prospecting tool by looking carefully at the type of fluids and mixings they recorded and especially by looking for H₂ and/or O₂ that indicate mineralization is in the vicinity. However, further studies on the migration of these gases and on simple detection methods are needed to test the efficiency of such a prospecting tool.

Acknowledgements

The authors acknowledge COGEMA for the sampling and the financial support of this study. Patrice Bruneton and Jean Mondy are thanked for their comments, discussions, and corrections. Xavier Moreau is thanked for its collaboration from Australia. Thérèse Lhomme is also thanked for carrying out the Raman analyses. The reviewers are greatly acknowledged for their corrections and comments.

References

- Cuney, M., Mathieu, R., 2000. Extreme light rare earth element mobilization by diagenetic fluids in the geological environment of the Oklo natural reactor zones, Franceville basin, Gabon. *Geology* 28, 743–746.
- Deckart, K., Renac, C., Kyser, T.K., submitted. Reassessment of the time of Oenpelli magmatism by Ar–Ar dating and its significance for spatially associated uranium mineralization, Pine Creek Basin, NT, Australia. *Economic Geology*.
- Dubessy, J., Audeoud, D., Wilkins, R., Kosztolanyi, C., 1982. The use of the Raman microprobe mole in the determination of the electrolytes dissolved in the aqueous phase of fluid inclusions. *Chemical Geology* 37, 137–150.
- Dubessy, J., Pagel, M., Beny, J.M., Christensen, H., Hickel, B., Kosztolanyi, C., Poty, B., 1988. Radiolysis evidenced by H₂–O₂ and H₂-bearing fluid inclusions in three uranium deposits. *Geochimica et Cosmochimica Acta* 52, 1155–1167.
- Dubessy, J., Poty, B., Ramboz, C., 1989. Advances in C–O–H–N–S fluid geochemistry based on micro-Raman spectrometric analyses of fluid inclusions. *European Journal of Mineralogy* 1, 517–534.
- Durak, B., Pagel, M., Poty, B., 1983. Températures et salinités des fluides au cours des silicifications diagénétiques d'une formation gréseuse surmontant un gisement d'uranium du socle:

- l'exemple des grès Kombolgie (Australie). *Comptes Rendus de l'Académie des Sciences*, Paris 296 (II), 571–574.
- Fabre, C., Boiron, M.C., Dubessy, J., Moissette, A., 1999. Determination of ions in individual fluid inclusions by laser ablation optical emission spectroscopy: development and applications to natural fluid inclusions. *Journal of Analytical Atomic Spectrometry* 14, 913–922.
- Fayek, M., Kyser, T.K., 1997. Characterization of multiple fluid-flow events and rare-earth-element mobility associated with formation of unconformity-type uranium deposits in the Athabasca Basin, Saskatchewan. *Canadian Mineralogist* 35, 627–658.
- Ferguson, J., 1980. Metamorphism in the Pine Creek Geosyncline and its bearing on stratigraphic correlation. In: Ferguson, A. (Ed.), *Uranium in the Pine Creek Geosyncline*. International Atomic Energy Agency, Vienna, pp. 91–100.
- Hanor, J.S., 1994. Origin of saline fluids in sedimentary basins. In: P.J. (Ed.), *Geofluids; Origin, Migration and Evolution of Fluids in Sedimentary Basins*. Geological Society Special Publication, pp. 151–174.
- Hedenquist, J.W., Reyes, A.G., Simmons, S.F., Taguchi, S., 1992. The thermal and geochemical structure of geothermal and epithermal systems: a framework for interpreting fluid inclusions data. *European Journal of Mineralogy* 4, 989–1015.
- Hoeve, J., Quirt, D., 1987. A stationary redox front as a critical factor in the formation of high grade, unconformity-type uranium ores in the Athabasca Basin, Saskatchewan, Canada. *Bulletin de Mineralogie* 110, 151–171.
- Hoeve, J., Sibbald, T.I.I., 1978. On the genesis of Rabbit Lake and other unconformity-type uranium deposits in northern Saskatchewan, Canada. *Economic Geology* 73, 1450–1473.
- Kish, L., Cuney, M., 1981. Uraninite–albite veins from the Mistamisk Valley of the Labrador Trough, Québec. *Mining Magazine* 44, 471–483.
- Komninou, A., Sverjensky, D.A., 1996. Geochemical modeling on the formation of an unconformity-type uranium deposit. *Economic Geology* 91, 590–606.
- Krylova, T.L., Aleshin, A.P., Chabiron, A., Pironon, J., Velichkin, V.I., Poty, B., Cuney, M., 2002. Uranium-bearing fluid composition on the Streltsovskoye and Antei deposits (Eastern Transbaikalia, Russia), Uranium deposits from their genesis to their environmental impact. *Praga*, 24–28.
- Kyser, T.K., Hiatt, E., Renac, C., Durocher, K., Holk, G., Deckart, K., 2000. Diagenetic fluids in paleo- and meso-proterozoic sedimentary basins and their implications for long protracted fluid histories. In: Kyser, K. (Ed.), *Fluids and Basin Evolution*. Short Course Series. Mineralogical association of Canada, Calgary, pp. 225–262.
- Ludwig, K.R., Grauch, R.I., Nutt, C.J., Nash, J.T., Frishman, D., Simmons, K.R., 1987. Age of uranium mineralization at the Jabiluka and Ranger deposits, Northern Territory, Australia: new U–Pb Isotope evidence. *Economic Geology* 82, 857–874.
- Maas, R., 1989. Nd–Sr isotope constrains on the age and origin of unconformity-type uranium deposits in the Alligator Rivers Uranium Field, Northern Territory, Australia. *Economic Geology* 84, 64–90.
- Mernagh, T.P., Wilde, A.R., 1989. The use of the laser Raman microprobe for the determination of salinity in fluid inclusions. *Geochimica et Cosmochimica Acta* 53, 765–771.
- Needham, R.S., 1988. Geology of the Alligator Rivers Uranium Field, Northern territory. *BMR Bulletin* 224, 96.
- Page, R.W., 1994. Katherine SD53-9-1,250 000 Geological map series explanatory notes. NTGS-AGSO.
- Pagel, M., Poty, B., Sheppard, M.F.S., 1980. Contribution to some Saskatchewan uranium deposits mainly from fluid inclusion and isotopic data. In: IAEA (Ed.), *Uranium in the Pine Creek Geosyncline*, Vienna, pp. 639–645.
- Poty, B., Leroy, J., Jachimovicz, L., 1976. Un nouvel appareil pour la mesure des températures sous le microscope: l'installation de la platine microthermométrique CHAIXMECA. *Bulletin de la SFMC* 99, 182–186.
- Rawlings, D.J., 1999. Stratigraphic resolution of a multiphase intracratonic basin system: the McArthur Basin, northern Australia. *Australian Journal of Earth Sciences* 46, 703–723.
- Robert, P., 1985. Histoire géothermique et diagenèse organique. *Bulletin des centres de recherches exploration–production Elf-Aquitaine*. Mem., vol. 8. Pau, 325 pp.
- Sweet, I.P., Brakel, A.T., Carson, L., 1999. The Kombolgie Subgroup—a new look at an old “formation”. *AGSO Research Newsletter* 30, 26–28.
- Walther, J.V., Helgeson, H.C., 1977. Calculation of the thermodynamic properties of aqueous silica and the solubility of quartz and its polymorphs at high pressures and temperatures. *American Journal of Science* 277, 1315–1351.
- Wilde, A.R., Mernagh, T.P., Bloom, M.S., Hoffmann, C., 1989. Fluid inclusion evidence on the origin of some Australian unconformity-related uranium deposits. *Economic Geology* 84, 1627–1642.
- Yanatieva, O.K., 1946. Polythermal solubilities in the systems $\text{CaCl}_2\text{--MgCl}_2\text{--H}_2\text{O}$ and $\text{CaCl}_2\text{--NaCl--H}_2\text{O}$. *Zhur. Priklad. Khim.* 19, 709–722.
- Ypma, P.J.M., Fuzikawa, K., 1980. Fluid inclusion isotope studies of the Nabarlek and Jabiluka uranium deposits, Northern Territory, Australia. In: IAEA (Ed.), *Uranium in the Pine Creek Geosyncline*, Vienna, pp. 375–395.
- Zhang, Y.G., Frantz, J.D., 1987. Determination of the homogenisation temperatures and densities of supercritical fluids in the system $\text{NaCl--KCl--CaCl}_2\text{--H}_2\text{O}$ using synthetic fluid inclusions. *Chemical Geology* 64, 335–350.