

Paleo-fluid composition determined from individual fluid inclusions by Raman and LIBS: Application to mid-proterozoic evaporitic Na–Ca brines (Alligator Rivers Uranium Field, northern territories Australia)

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Abstract

Detailed determination of the composition of individual fluid inclusions in the H₂O–NaCl–Ca(Mg)–Cl₂ system from microthermometry data may be difficult because (i) the melting of salt hydrates is often unclear, (ii) salts or salt hydrates are often metastable, and (iii) eutectic temperatures are often difficult to relate precisely to a unique salt–water system. These problems can be circumvented by using a Raman microprobe to identify the salt hydrates and to measure the chlorinity, by using Laser Induced Breakdown Spectroscopy (LIBS) to determine cation ratios, and by cross-checking the data from these independent techniques at each step in the determination of the fluid inclusion composition. Data from individual inclusion analysis are then completed by crush–leach technique data on bulk samples.

This methodology was applied to a case study, the mineralized faults and associated breccia located in the Alligator Rivers Uranium Field (middle Proterozoic Kombolgie Subgroup, Northern Territory, Australia). Faults are cemented by euhedral quartz containing a variety of fluid inclusions with a wide range of ice-melting temperatures, from near 0 °C down to about –50 °C. The approach has permitted the identification of three types of fluids: an Na-rich brine with variable Mg concentrations, a Ca-rich brine with low Mg concentrations, and a lower salinity fluid. The Ca and Na-brines mixed with each other and a less saline end-member. On the basis of Cl/Br and cation ratios, the Na-brine is interpreted as a primary brine, resulting from the evaporation of seawater. It is inferred that the Na-brine evolved chemically during its interaction with the Ca-rich lithologies from Proterozoic basement, forming subsequently a Ca-brine through Na–Ca exchange reactions. Thus, the fault system, which affects both the base of the Kombolgie sandstone and its basement, represents active drainage zones where different fluid reservoirs were connected, and thus a place where fluid mixing was highly favored.

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Keywords: Fluid inclusions; Raman analysis; LIBS; System NaCl–CaCl₂–H₂O; Alligator Rivers Uranium Field

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1. Introduction

Formation waters in sedimentary basins often contain significant amounts of cations other than Na^+ , such as Ca^{2+} , Mg^{2+} , Li^+ , as shown by the aqueous fluids from oil fields, evaporitic strata and deep basins (Carpenter et al., 1974; Fisher and Kreitler, 1987; Kharaka et al., 1987; Wilson and Long, 1993; Fontes and Matray, 1993; Hyeong and Capuano, 2001). For paleofluids trapped within fluid inclusions, bulk analyses are generally obtained by crushing and leaching the host minerals (Bottrell et al., 1988; Banks and Yardley, 1992; Gleeson et al., 2001), a procedure that is meaningful when there is only one dominant fluid population. Microthermometry gives information on the salinity of the fluid inclusion (most frequently expressed as equivalent wt.% eq. NaCl or wt.% eq. CaCl_2), but it does not always enable, a detailed reconstruction of the composition of individual fluid inclusions in the H_2O –NaCl– $\text{Ca}(\text{Mg})\text{Cl}_2$ systems for two reasons: (i) the exact melting of salt hydrates is often difficult to observe, and thus the chronology of phase transitions cannot be established, and (ii) metastability of salts or salt hydrates often renders the use of phase transitions problematic (Roedder, 1984; Dubessy et al., 1992). These problems can be circumvented by using Raman microprobe to identify the salt hydrates and to estimate the chlorinity (Mernagh and Wilde, 1989; Dubessy et al., 2002), by using Laser Induced Breakdown Spectroscopy (LIBS) to determine cation ratios (Fabre et al., 1999), and using microthermometry that remains indispensable to exclude aberrant results due to, invisible-to-the-eye, trapped solids within the fluid inclusion, and to observe the temperature of last melting. Cross-checking the data from these independent techniques at each step in the determination of the fluid inclusion composition allows the composition of the fluid to be validated.

This methodology was applied to a case study, located in the middle Proterozoic Kombolgie Subgroup, along the northern margin of the McArthur basin, Northern Territory, Australia, where brine mixing was previously deduced from microthermometric data (Derome et al., 2003). Several earlier fluid inclusion studies of quartz cements (in sandstones, and faults) in middle Proterozoic sedimentary basins described a wide range of ice-melting temperatures, from near 0 °C down to about –50 °C, initially interpreted by Durak et al. (1983) as due to the presence of Ca^{2+} , Mg^{2+} and Li^+ in addition to Na^+ on the basis of microthermometric data.

Microthermometric investigations of fluids from seven localities have shown the existence of brines, with similar features to those cited above, intimately mixed in euhedral quartz crystals (Derome et al., 2003). These euhedral

quartz crystals contain fluid inclusions ($>20\text{ }\mu\text{m}$), that are suitable for in-situ analysis. The present study has two goals: (1) to demonstrate the efficiency of cross-checking different independent analytical techniques to obtain the composition of individual fluid inclusions and (2) to apply this method to natural samples in order to determine the composition and the hydrodynamic regime of paleofluids in the Kombolgie Subgroup, near the unconformity with the Paleoproterozoic basement. For the latter objective, additional data for the trace element content (Sr, Ba, Li) was obtained using a new configuration of the LIBS technique (Fabre et al., 2005). The crush–leach technique was used to determine the halogen molar ratios, and to provide additional data on trace element concentrations.

2. Analytical methods

Low temperature microthermometry was performed on a Chaix-Meca cooling stage (Poty et al., 1976) mounted on an Olympus optical microscope equipped with a $\times 80$ objective. The eutectic, ice and hydrate melting temperatures (respectively T_e , $T_{m_{ice}}$, $T_{m_{hyd}}$) were measured. Homogenization temperatures (T_h) were measured using a USGS-Fluid inc. cooling–heating stage on the same inclusions previously studied. The stages were calibrated with melting-point standards at $T > 25\text{ }^\circ\text{C}$ and natural and synthetic fluid inclusions at $T < 0\text{ }^\circ\text{C}$. The rate of heating was monitored in order to obtain an accuracy of $\pm 0.2\text{ }^\circ\text{C}$ during freezing, $\pm 1\text{ }^\circ\text{C}$ below 200 °C. Due to the difficulties in observing the first melting (eutectic) or hydrate melting in the presence of ice, the uncertainty of T_e and $T_{m_{hyd}}$ may reach $\pm 5\text{ }^\circ\text{C}$ and even larger for small fluid inclusions ($\sim 5\text{ }\mu\text{m}$). A DILOR LABRAM Raman spectrometer was used for chlorinity measurements using the procedure described in Dubessy et al. (2002) on the same inclusions studied by microthermometry. Chlorinity is given in mol/kg H_2O . This technique was also used for the identification of salt hydrates (Dubessy et al., 1982; Bakker, 2001).

LIBS was used to determine the cation ratios of individual fluid inclusions that do not contain solids. The excitation source was a Nd-YAG (266 nm) laser focused onto the fluid inclusion through a Cassegrain-type optical microscope (Dilor, Lille, France). The emission lines of the plasma produced by the ablation, are characteristic of the dissolved cations. These were directly analyzed by a spectrometer with a multichannel detector (Boiron and Dubessy, 1994; Fabre et al., 1999). This method mainly detects Na^+ , Ca^{2+} , Mg^{2+} , K^+ , and Li^+ . The results are given as cation mole ratios calculated from the relative intensities of their emission lines calibrated with standards of known composition (Fabre et al., 1999). The detection limits range from 10 ppm for Ca to 100 ppm for K (Fabre,

2000). As this technique is destructive, it is used only when all the other techniques have been applied to the same individual inclusion.

Crush–leach analysis was performed using the method described in Banks et al. (2000). Approximately 1 g of cleaned quartz was crushed and leached with an acidified La-solution for cation analysis and doubly distilled water for anion analysis. Cations were analyzed by ICP-MS and anions by ion chromatography. Both types of solution were also analyzed by flame emission spectroscopy for Na, K and Li.

2.1. Analytical procedure

Phase changes (T_e , $T_{m_{ice}}$, $T_{m_{hyd}}$) were carefully observed in fluid inclusions by cyclic freezing (Haynes, 1985) during the cooling runs. Two scenarios were distinguished (Fig. 1):

- (i) When salt hydrates were observed within fluid inclusions, successive heating and freezing runs were performed to induce the growth of a well-crystallized solid. The identification was carried out by the Raman microprobe at $-175\text{ }^{\circ}\text{C}$ (Dubessy et al., 1982). Then to obtain the relative proportion of each salt, the melting temperatures of ice and/or hydrate were plotted in the appropriate phase diagram

(Haynes, 1985; Vanko et al., 1988; Zwart and Touret, 1994). For the present study, the H_2O – NaCl – CaCl_2 ternary diagram was used (Yanatieva, 1946; Schiffries, 1989; Oakes et al., 1990), and the data from the ice and hydrohalite melting temperature, the nature of which is determined by Raman at low temperature (1 and 2 in Fig. 2) and the relative proportions are deduced from it.

- (ii) When hydrates could not be observed, the Raman microprobe was used to determine the chlorinity of the liquid phase from the shape of the stretching–vibration band of water (Dubessy et al., 2002). Analysis was performed at room temperature with a circularly depolarized laser beam and with the quartz host-crystal of the inclusions oriented in one of its extinction positions. Then, the molar cation ratios were determined from the LIBS analyses.

2.2. Reconstruction of the composition of individual fluid inclusions: LIBS and Raman techniques

The chlorinity and cation ratios, determined from Raman and LIBS analysis, were combined to calculate the salt composition of individual fluid inclusions. The LIBS cationic ratios are referred to as R1 ($\text{Ca}^{2+}/\text{Na}^{+}$) and R2 ($\text{Mg}^{2+}/\text{Ca}^{2+}$) in the following paragraph. Considering that the main cations are Na^{+} , Ca^{2+} and Mg^{2+} and

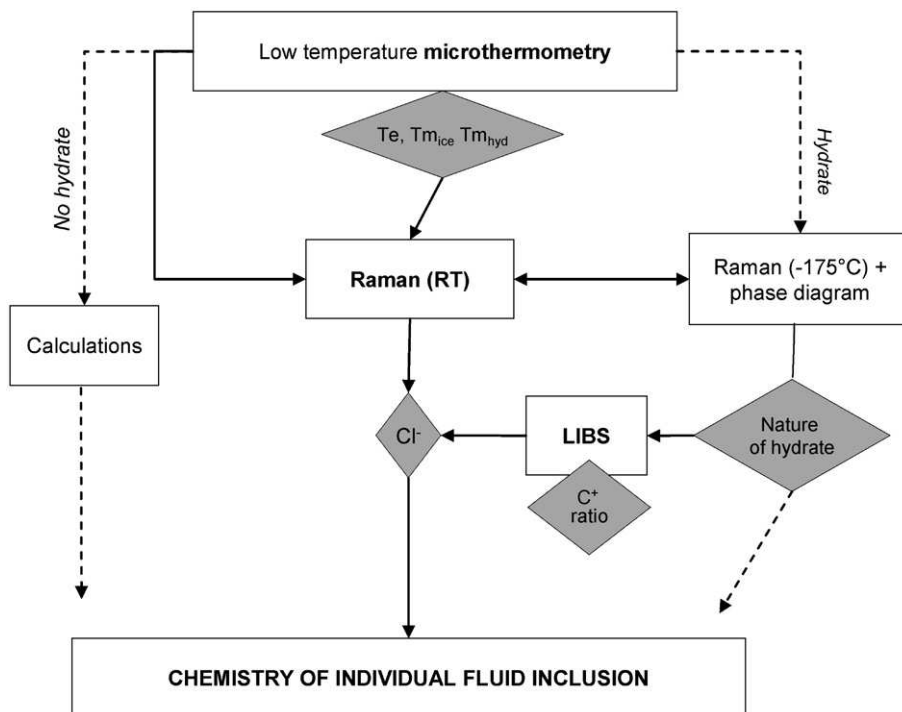


Fig. 1. Flow diagram of a fluid inclusion study using microthermometry, Raman micro-spectroscopy and LIBS analyses (RT:room temperature).

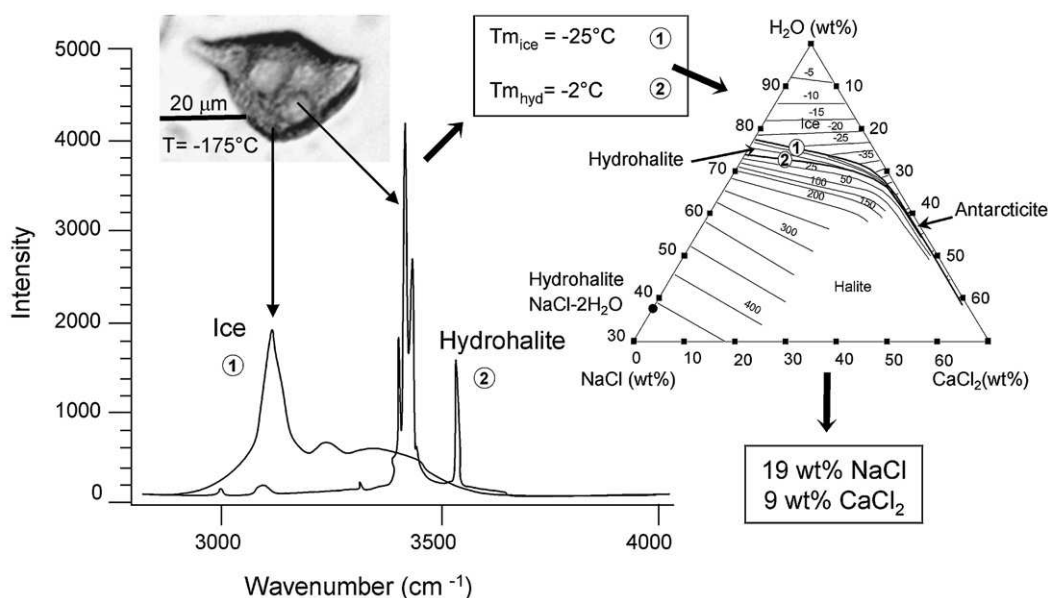


Fig. 2. a—Raman spectra of ice (1) and hydrohalite NaCl–2H₂O (2) obtained within a fluid inclusion at –180 °C, after sequential freezing. Ice melts at –25 °C and hydrohalite melts at –2 °C; b—phase diagram of the H₂O–NaCl–CaCl₂ system (modified from Yanatieva, 1946; Oakes et al., 1990). Point (1) corresponds to the ice melting temperature of the fluid inclusion. Point (2) is the hydrohalite melting temperature (final melting). The position of the point (2) represents the composition of the fluid inclusion at room temperature.

that the major anion is Cl[–] for this study, as no K⁺ was detected, the following charge-balance equation is used: $m\text{Cl}^- = m\text{Na}^+ + 2m\text{Ca}^{2+} + 2m\text{Mg}^{2+}$, where $m\text{Ca}^{2+}$ and $m\text{Mg}^{2+}$ are subsequently replaced by $m\text{Na}^+ \times R1$ and $m\text{Na}^+ \times R1 \times R2$, respectively. Thus, the composition of each individual fluid inclusion is calculated from the following equations. Results are given in mol/kg H₂O:

$$m\text{NaCl} = \frac{m\text{Cl}^-}{1 + 2 \times R1 \times (1 + R2)} \quad (1)$$

$$m\text{CaCl}_2 = m\text{NaCl} \times R1 \quad (2)$$

$$m\text{MgCl}_2 = m\text{CaCl}_2 \times R2 \quad (3)$$

where $m\text{Cl}^-$ is the chlorinity deduced from Raman analysis, and $R1 = \text{Ca}/\text{Na}$; $R2 = \text{Mg}/\text{Ca}$, from LIBS.

The compositions were also calculated in wt.%, using Eq. (4), to enable comparison with the microthermometric data reported in the H₂O–NaCl–CaCl₂ phase diagram (Fig. 2).

$$\text{NaCl (wt.\%)} = \frac{m\text{NaCl} \times 58.4}{(1000 + m\text{NaCl} \times 58.43 + m\text{CaCl}_2 \times 111 + m\text{MgCl}_2 \times 95.21)} \times 100 \quad (4)$$

The same relation was used to calculate the concentration CaCl₂ and MgCl₂ in wt.%.

2.3. Calculations based on microthermometric measurements

As all fluid inclusions in the present study have T_e close to –52 °C, the dominant salts in solution are most probably NaCl and CaCl₂ (Yanatieva, 1946). Therefore, when hydrohalite melting was not observed, the composition of individual fluid inclusions was estimated, approximately, by treating them as simple binary H₂O–NaCl or H₂O–CaCl₂ systems depending on whether the $T_{m\text{ice}}$ of the fluid inclusion is above or below –21 °C.

3. A case study: the Middle Proterozoic McArthur basin

3.1. Location and geological context

The study area (Northern Territory, Australia) is located about 300 km to the east of Darwin, and consists of a thick (presently 1500–1800 m) un-metamorphosed detrital sequence (the “Kombolgie subgroup”: Sweet et al., 1999) of epicontinental clastic sediments from the Cahill formation that unconformably overlies the Archean to lower Proterozoic crystalline and metamorphic basement rocks (Needham, 1988). The Kombolgie subgroup is composed mostly of continental sandstones deposited near coastal areas, between 1822 and 1720 Ma (Sweet

et al., 1999). It probably reached a thickness of about 4.5 km and the pressure at the base of the basin was estimated to 1125 ± 250 bar (Derome et al., 2003). The study area hosts world-class unconformity-type uranium deposits that mainly occur at the western margin of the Arnhem Land Plateau (northwest McArthur Basin; Sweet et al., 1999), and are hosted close to the unconformity but within the basement in the Alligator Rivers Uranium Field (ARUF). Faults and breccias studied in the present paper represent the upper extension of fault systems affecting the basement as well as the overlying sandstones as shown in Fig. 3a and b, and are characterized by similar fluid types to those recognized within the basement (Derome et al., 2003). All uranium deposits in the Alligator Rivers Uranium Field, except Nabarlek, are located in the Lower Cahill Formation. 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 Koongarra deposits have been dated between 1600 and 1650 Ma using Sm–Nd and Rb–Sr methods on uraninites (Maas, 1989), and more recently ca. 1680 Ma (Polito et al., 2005) using U–Pb on uraninite from Jabiluka.

In quartz breccia zones related to fault affecting both the basal Kombolgie sandstones and in the basement rocks, previous studies have shown a rather similar sequence of silicification of sandstones and fault cementation, probably in relation with desilicification

processes related to water–rock interactions during the main stage of U-deposition, as described in detail in unconformity related Canadian deposits (Lorilleux et al., 2002). In several localities, e.g. 10 km south of the Nabarlek deposit, at North Caramal and Caramal (and U65) U-showings, South Horn and Jabiluka U-deposit, several quartz generations were distinguished: i) Q1: diagenetic epitaxial quartz overgrowths on detrital quartz grains that correspond to the first stage of the sandstone cementation, Q2: quartz filling intergranular voids that correspond to pervasive silicification representative of a later stage of cementation probably coeval of Q3, Q3: millimetres to several centimetres long drusy quartz crystals cementing breccia bodies that crosscut the sandstones corresponding to the third stage of sandstone silicification, linked to a fracturation event and Q4: euhedral amethyst quartz overgrowths on Q3 that represents the latest silicification event observed in the studied samples.

3.2. Analyzed samples and fluid inclusion petrography

Hydraulic breccias, which are especially frequent along faults affecting both the bottom of the basin and the basement, were sampled at North Caramal (samples NCA02 and NCA03), and Caramal (CA001) on outcrops at 20 to 30 m above unconformity (Fig. 3a and b). Breccias are formed of angular blocks of

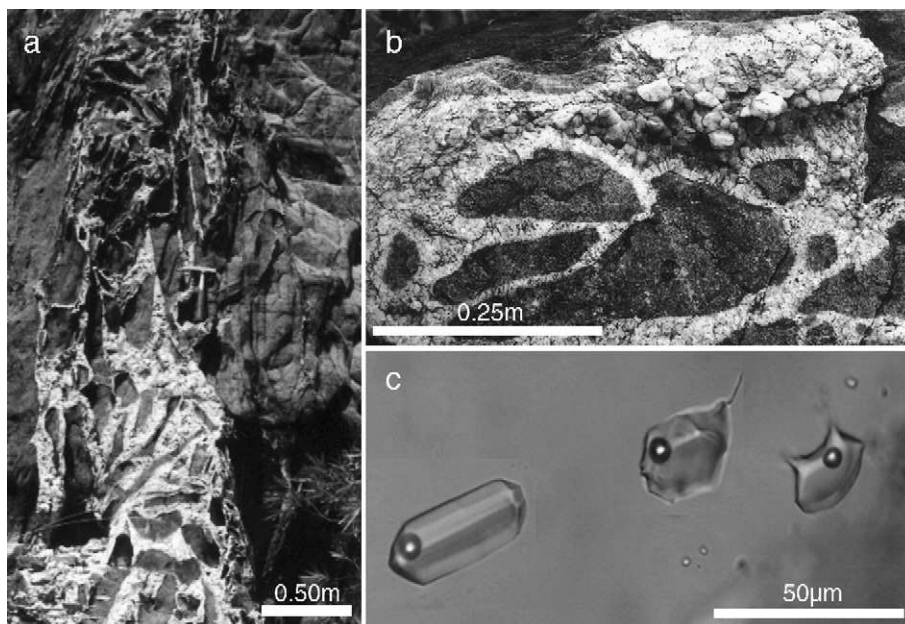


Fig. 3. a—"Vein-type" hydraulic breccia crosscutting the Kombolgie sandstones and cemented by drusy quartz, North Caramal area, McArthur Basin (Northern Territory, Australia). b—Detail of drusy quartz and breccia. The quartz crystals are commonly 2–3 cm long. c—Large fluid inclusions without solids in drusy quartz, ideal for LIBS analysis.

sandstones cemented by nice euhedral drusy quartz crystals of rather exceptional size up to 10 cm at their base. Drusy quartz crystals correspond to the Q3 stage, and contain the three main fluid types identified in the area: two brines and a lower salinity fluid which shows clear evidence of mixing with the brines (Derome et al., 2003). For comparison, one sample (denoted RAN3) was taken in the Ranger 3 open pit, 10–20 m above the unconformity and about 20 to 50 m above the main U-ore zone. Other samples, already described in Derome et al. (2003), were analyzed by the crush–leach method (Nabarlek, and U65 close to Caramal and Jabiluka) for comparison. Microthermometry and fluid petrography on these samples is published in Derome et al. (2003). The mixing of the fluids within the breccia is considered to have produced quartz precipitation, and is supported by the following arguments :

- quartz Q3 hosts inclusions of the three fluid inclusion types, which are located within the same growth band in a single macroscopic quartz crystal, with no clear chronological relationships, or within pseudo-secondary inclusions (cracks of small size cutting only one

growth band or limited part of the crystal). There is a clear lack of any late fluid inclusion planes which could have indicated the healing of late micro-cracks and a possible contamination of fluid inclusions, or the mixing of two distinct fluid populations related to two separate fluid events (Fig. 3c).

- the population of inclusions in a single growth band from Q3 at North Caramal are characterized by a wide range of $T_{m_{ice}}$ and a small range of T_h . T_m – T_h pairs are similar to the trends described in other deposits. The occurrence of fluids with a wide range of salinities was determined in previous fluid inclusion studies carried out on the basement rocks (Ypma and Fuzikawa, 1980; Wilde et al., 1989), and silicified Kombolgie sandstones. The clear similarities in the fluid types allowed Derome et al. (2003) to relate this fluid event to the major stage of brine circulation related to the formation of the major U-deposits. Twelve inclusions related strictly to U-ore deposition were studied by Polito et al. (2005), at Jabiluka, and are interpreted as chemically distinct from fluid inclusions studied by Wilde et al. (1989) or Derome et al. (2003). These fluid inclusions have however features intermediate between the Na-

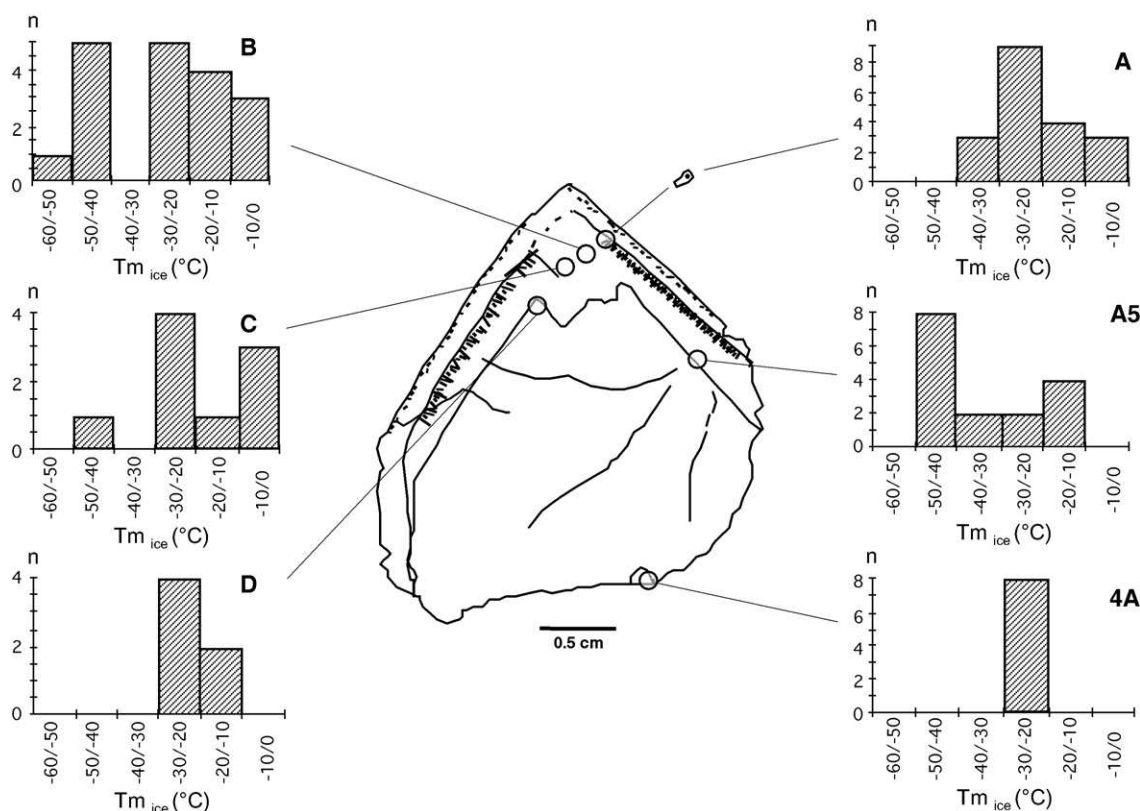


Fig. 4. Histograms of ice melting temperature in six zones a single quartz crystal from North Caramal (sample NCA02): inclusions along growth band (D, A5, 4A), and pseudo secondary inclusions (C, B), and a late growth band (A).

Table 1

Summary of results from microthermometry, Raman and LIBS analyses of individual fluid inclusions, and their corresponding compositions

Locality	Samples	IF N°	Te	Microthermometry			Composition (from phase diagram)			Raman analyses	LIBS	Composition from Raman and LIBS (wt.%)				
				Tm _{ice} (°C)	Tm _{hyd} (°C)	Th (°C)	NaCl (wt.%)	CaCl ₂ (wt.%)	H ₂ O (wt.%)	Cl (mol/ kg H ₂ O)	Na/Ca (1/R1)	Ca/Mg (1/R2)	NaCl	CaCl ₂	MgCl ₂	H ₂ O
<i>Ca-rich brine</i>																
North Caramal	NCA02	A5-9	−61	−44		98		28.9	71.1	6	0.2		2.1	23	0	74.9
	NCA02	A-18	−57	−39		110		27.9	72.1	5.7	0.1		1.2	22.9	0	75.9
	NCA02	B-9	−61	−43		103		28.7	71.3	5.5	0.1		0.8	22.6	0	76.6
	NCA02	B-5	−61	−42		103		28.4	71.6	5	0.1		1.3	20.5	0	78.2
Caramal	CA001	2	−55	−27	−0.9	116	16	11	73	5.6	1.1	10	8.1	14	1.7	76.2
	CA001	1	−55	−28	−1	115	14.5	12.5	73	5.1	1.1		8.2	14.2	0	77.6
<i>Na-rich brine</i>																
North Caramal	NCA02	A-1	−39	−27	8	122	16.5	11	72.5	5.7	2.5	1	10.2	7.2	6.2	76.4
	NCA02	4A-7	−59	−26	−5	117	16.5	10	73.5	5.6	5.0		18.8	5.7	0	75.6
	NCA02	B-21	−86	−47		101		29.5	70.5	5.5	2.5		13.2	10.7	0	76.1
	NCA02	B-2	−56	−45		115		29.1	70.9	6	3.3		16.8	8.8	0	74.4
	NCA02	B-12	−68	−29		114		25.4	74.6	4	3.3		11.8	6.8	0	81.3
	NCA02	C-3	−55	−26		110		24.4	75.6	5	5.0	3	14.6	6.2	1.3	77.9
	NCA02	C-1	−51	−25		107		24.1	75.9	4.8	5.0	3	14.2	5.7	1.4	78.6
	NCA03	D-1	−68	−25	−3	97	19.5	6.5	74	5	10.0		18.2	4.2	0	77.6
	NCA03	C-7	−64	−26		118		24.4	75.6	5.5	5.0		17.6	6.4	0	75.9
	NCA03	B-4	−74	−28		127		25.3	74.7	5.3	5.0	10	17.5	5.6	0.3	76.6
Caramal Ranger	NCA03	B-5	−74	−28		128		25.3	74.7	5.3	2.5	5	11.6	9.6	1.8	77
	CA001	4	−55	−28	2	121	15	12.5	72.5	5	3.3		14	8.3	0	77.7
	RAN3	4A-2	−59	−21	−23.9		15.5	5.5	79	3.9	5.0		13.9	4.5	0	81.6
<i>Brackish water</i>																
North Caramal	NCA02	A13	−55	−11		130	15		85	3.2	10.0		13.2	2.4	0	84.4
	NCA02	A5-4	−58	−15		124	18.5		81.5	3.4	0.1		0.9	15	0	84.1
	NCA02	B-4	−50	−11		128	15.2		84.8	3	5.0		10.8	3.9	0	85.3
	NCA02	A5-7	−58	−12		126	16.4		83.6	4.3	1.0		6.7	12.8	0	80.5
	NCA02	B-7	−50	−11		130	15.5		84.5	3	3.3		9.3	5.4	0	85.3
	NCA02	A-8	−46	−10		135	13.8		86.2	2.1	5.0		7.7	3.1	0	89.2
	NCA02	C-8	−48	−8		140	12.3		87.7	1.8	2.5	10	4.9	4	0.4	90.8
	NCA02	B-14	−42	−4		150	6.3		93.7	1	3.3		3.3	2.2	0	94.6
	NCA03	C-1	−39	−8		127	12.1		88	1.8	3.3	5	5.5	3.2	0.6	90.8
Caramal	CA001	5	−40	−8.5		157.4	12.3		87.7	2.2	10.0		9.7	1.6	0	88.7
	CA001	3	−37	−7	−30	126	4	6	90	1.8	1.4		3.9	5.3	0	90.7
Ranger	RAN3	4A-6	−55	−19	−22.9		13.5	9	77.5	3.8	1.7		8.4	9.4	0	82.2
	RAN3	4A-32	−47	−6			9.2		90.8	1.5	10.0		6.9	1.1	0	92

Inclusion numbers for sample NCA02 from North Caramal refer to zones indicated in Fig. 4 (A, B, C, A5, 4A).

brine and the less saline fluid defined by Derome et al. (2003). They have eutectic temperatures around -35 ± 5 °C, and final melting from -18 °C to -4 °C, but could not be homogenized due to the possible presence of gases produced by radiolysis (large vapor bubble) although no Raman data are available to confirm this (Polito et al., 2005). Such fluids are compatible with the fluid types described in all localities, but represent only a part of the fluid system.

Inclusions in quartz Q3 from the Caramal area (North Caramal and Caramal) are quite large, and are clearly

hosted in growth bands within the euhedral quartz. They are considered as primary fluid inclusions and have much larger sizes (20–60 μm) than all other inclusions described within the silicified sandstones or the altered basement rocks. They often possess an irregular or rectangular shape, with their elongation oriented perpendicular to the growth zones of the drusy quartz. They were considered as representative of the main process of quartz deposition, and provided adequate material for a detailed study of the compositions of the main fluid types related with the U-mineralization process. Fluid inclusion planes from the mineralized basement are less favorable because

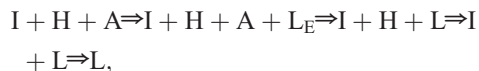
of their smaller size and the frequent presence of trapped solids. A detailed study was thus carried out on the two representative quartz crystals from the same breccia at North Caramal, where a set of about 25 large solid-free fluid inclusions (Fig. 4, Table 1) were carefully selected with the aim of performing in-situ analysis. Comparisons with representative inclusions from Caramal and Ranger U-deposit were also carried out. The fluid inclusion study was performed on doubly-polished sections of 100 μm thickness. At room temperature, all the fluid inclusions contain a liquid phase and a vapor bubble (the bubble occupies approximately 15 vol.% of the inclusions).

3.3. Fluid inclusion data

In all the fluid inclusions, eutectic melting occurs between $-40\text{ }^{\circ}\text{C}$ and $-74\text{ }^{\circ}\text{C}$ (Table 1), which indicates the presence of divalent cations, Ca^{2+} and Mg^{2+} in addition to Na^{+} , as confirmed by LIBS. Two distinct types of behavior were distinguished during the cooling runs, depending on the melting sequences.

- (i) In most fluid inclusions, the last phase to melt was ice. This corresponds to type 1a of Schiffries

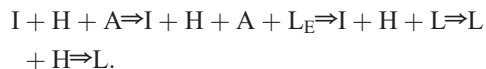
(1989). The melting sequence in presence of a vapor phase was the following:



where I = Ice, H = hydrohalite, A = antarcticite, L_E = eutectic liquid, and L = Liquid.

In most cases, only the eutectic melting and the melting of ice were observed. Tm_{ice} was between $-47\text{ }^{\circ}\text{C}$ and $-2\text{ }^{\circ}\text{C}$. However, in some rare fluid inclusions (denoted 1a'), Tm_{hyd} (identified by Raman microprobe) was occasionally observed between $-30\text{ }^{\circ}\text{C}$ and $-24\text{ }^{\circ}\text{C}$, and Tm_{ice} was between $-21\text{ }^{\circ}\text{C}$ and $-7\text{ }^{\circ}\text{C}$.

- (ii) Hydrohalite was observed as the last phase to melt in a few of fluid inclusions, this succession corresponds to the type 1b of Schiffries (1989):



In these fluid inclusions, Tm_{hyd} was between $-5\text{ }^{\circ}\text{C}$ and $+8\text{ }^{\circ}\text{C}$ and Tm_{ice} between $-28\text{ }^{\circ}\text{C}$ and $-25\text{ }^{\circ}\text{C}$.

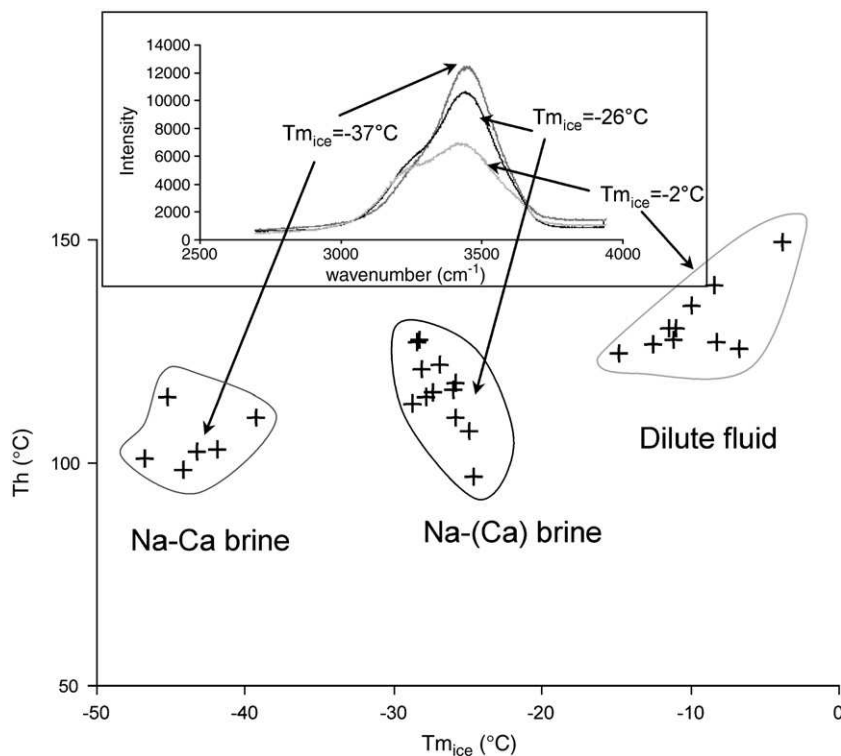


Fig. 5. Raman spectra of water, at room temperature, for fluid inclusions with different salinities ($\text{Tm}_{\text{ice}} = -35; -25; -10\text{ }^{\circ}\text{C}$) corresponding to the three populations of fluids distinguished on the basis of microthermometry (sample from North Caramal area).

In a few fluid inclusions, there was evidence of metastability. During the first low temperature measurement $T_{m_{ice}}$ was observed between $-30\text{ }^{\circ}\text{C}$ and $-40\text{ }^{\circ}\text{C}$. However, after repeating the measurements 3 or 4 times, hydrohalite finally nucleated and melted between $-5\text{ }^{\circ}\text{C}$ and $+5\text{ }^{\circ}\text{C}$, after ice. In such rare cases the $T_{m_{ice}}$ was close to $-25\text{ }^{\circ}\text{C}$.

All the inclusions homogenized to the liquid phase between $97\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$. The microthermometric data are presented in Table 1 and Fig. 5, and grouped according to the Raman spectra typical of the three salinity ranges. This diagram shows that the fluid inclusions with the highest salinity (i.e. the lowest $T_{m_{ice}}$) have the lowest homogenization temperatures. Although these data include different samples, this observation is repeated within single growth zones in individual quartz crystals (Dubessy et al., 2003), and is repeated on a district scale of 50 km (Derome et al., 2003).

3.4. LIBS and Raman analyses

The composition of the individual fluid inclusions previously studied by microthermometry was obtained by combining the chlorinity values deduced from Raman analysis with the cation ratios obtained by LIBS. The chlorinity obtained of the fluid inclusions is between 1 and 6 mol/kg H_2O . No gas could be detected quantitatively (no hydrate). Only traces of N_2 , or CH_4 were occasionally detected in inclusions.

A representative LIBS spectrum is shown in Fig. 6 for a fluid inclusion from Caramal (Na–Ca brine, with significant concentrations of Li, and Sr). LIBS analyses revealed the presence of Na and Ca in all fluid inclusions, as well as Mg, and in minor amounts Li, Sr, and occasionally Ba (Fig. 6). K was not detected using LIBS analysis due to the low response of the detector at its

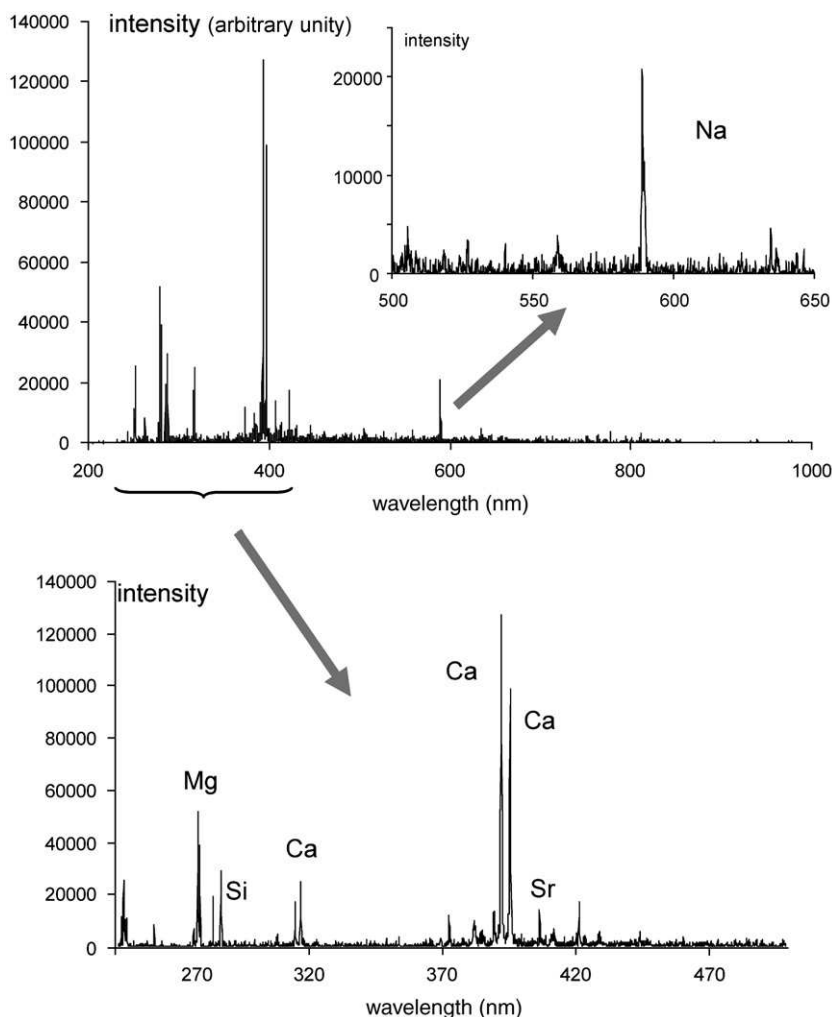


Fig. 6. LIBS spectra of Na–Ca–Li–Sr bearing fluid inclusions, with enlargements of two spectral ranges showing peaks for Mg, Ca, Sr and Na (North Caramal sample).

wavelength. Mg concentrations are distinctly different in the Na and Ca brines, and have a large degree of scatter. The molar Na/Ca ratio is between 0.1 and 10 and Ca/Mg is between 1 and 10 (Table 1). Li, Sr and Ba were detected in the two brines, but their concentrations were not determined quantitatively.

3.5. Composition of the paleofluids

The bulk composition of each fluid inclusion was first calculated from the ice melting temperature or from the combination of ice and hydrate melting temperatures. When no hydrohalite was observed, the salinity of inclusions with $T_{m_{ice}}$ above $-21\text{ }^{\circ}\text{C}$ was estimated at between 6 and 18 wt.% NaCl. The salinity of fluid inclusions with $T_{m_{ice}}$ below $-21\text{ }^{\circ}\text{C}$ was estimated to be between 28 and 30 wt.% CaCl_2 when interpreted in the $\text{CaCl}_2\text{--H}_2\text{O}$ system (North Caramal sample). These results are summarized in Table 1, but they must be considered as approximations. The latter are only reported in Fig. 7a to show the necessity of complementary investigation by LIBS which is, in the preceding cases, the only technique providing the quantitative Ca/Na ratios for individual inclusions. Besides, when both ice and hydrohalite melting are observed (diamonds in Fig. 7a), the estimates from microthermometry presented in the ternary phase diagram are close to those deduced from LIBS and Raman analysis (Fig. 7b).

Coupled sets of interpreted Raman and LIBS data (chlorinity, cation ratios), are presented in Table 1. Magnesium chloride was detected only in fluid inclusions

whose CaCl_2 content does not exceed 14 wt.%, indicating that magnesium is preferentially within the sodium-rich fluid. The compositions calculated in wt.% using Eq. (4) are presented in an $\text{H}_2\text{O--NaCl--CaCl}_2$ ternary diagram on the basis of microthermometry and LIBS–Raman analyses (Fig. 7b). This figure shows three end-members co-existing within the ternary system. They are represented by the following range of compositions:

- A calcium-rich brine, with about 1–8 wt.% NaCl + 14–23 wt.% CaCl_2 and no detectable MgCl_2 with the exception of one inclusion. This end-member primarily corresponds to fluid inclusions with $T_{m_{ice}}$ below about $-30\text{ }^{\circ}\text{C}$ when no hydrohalite is observed (Table 1).
- A sodium-rich brine, with about 10–19 wt.% NaCl + 4–11 wt.% CaCl_2 + 0–6 wt.% MgCl_2 . This type corresponds to fluid inclusions with $T_{m_{ice}}$ of about -21 to $-28\text{ }^{\circ}\text{C}$ in most cases and also to those in which hydrohalite melting was observed after $T_{m_{ice}}$.
- An Na–Ca–Mg fluid, which contains about 3–13 wt.% NaCl + 1–13 wt.% CaCl_2 + 0–0.6 wt.% MgCl_2 . This fluid corresponds to fluid inclusions with $T_{m_{ice}}$ ranging from -6 to $-15\text{ }^{\circ}\text{C}$.

4. Crush–leach analyses and $\delta^{18}\text{O}$

The reconstructed fluid composition calculated from crush–leach analyses and using the average salinity deduced from microthermometry and Raman spectroscopy is reported in Table 2. Comparisons have been made with samples from Nabarlek, U65 and South

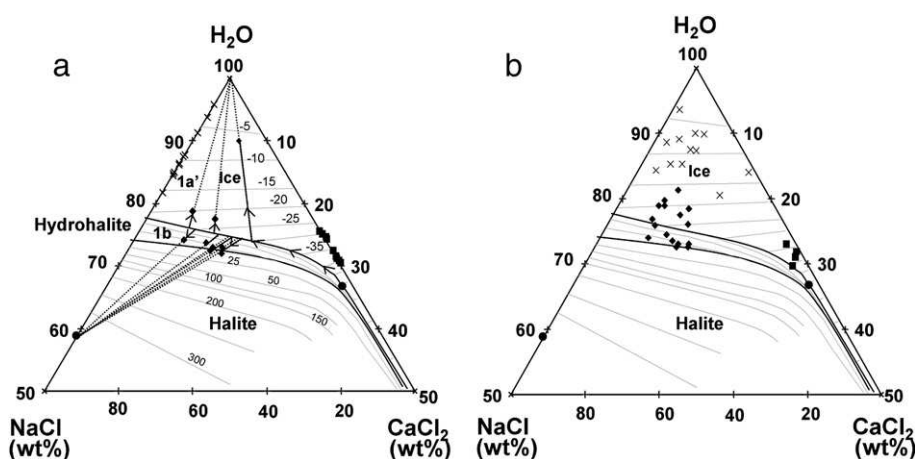


Fig. 7. The composition of individual fluid inclusions deduced from microthermometric measurements (a) and Raman-LIBS data (b) is plotted in a $\text{H}_2\text{O--NaCl--CaCl}_2$ (wt.%) ternary diagram. Three end-members are distinguished: an Na-rich brine (with low amounts of Ca), a Ca-rich brine (with low amounts of Na) and an Na-fluid. Crosses represent the Na-fluid for which the composition was calculated from $T_{m_{ice}}$ assuming the fluid belongs to the $\text{H}_2\text{O--NaCl}$ binary system ($T_{m_{ice}}$ above $-11\text{ }^{\circ}\text{C}$); full squares represent the composition for Ca-dominated brines (fluid inclusions with $T_{m_{ice}}$ below $-21\text{ }^{\circ}\text{C}$) and open diamonds correspond to the Na-rich brine for which the composition was determined from $T_{m_{ice}}$ and $T_{m_{hyd}}$, assuming the fluid belongs to the $\text{H}_2\text{O--NaCl--CaCl}_2$ system (Fig. 6a).

Table 2

Composition of Kombolgie fluids in mmol/kg H₂O

Locality	Sample	Na	K	Li	Ca	Mg	Cl	Br	SO ₄	Na/ K	Na/ Li	Na/ Ca	Na/ Mg	Na/ Br	Ca/ Mg	Cl/ Br	Cl/ SO ₄
Nabarlek	97-NAB-02-1	242	20	1	271	199	1262	8	5	12.1	242	0.9	1.2	30	1.4	158	252
	97-NAB-02-2	960	78	11	n.a.	n.a.	5198	35	22	12.3	87			27		149	236
	NAB-03	525	64	23	305	114	1306	6	33	8.2	23	1.7	4.6	88	2.7	218	40
North Caramal	NCA-02-1	1247	189	28	1569	189	6475	42	57	6.6	44	0.8	6.6	30	8.3	154	114
	NCA-02-2	1827	286	56	n.a.	n.a.	6013	40	92	6.4	33			46		150	65
Caramal	CA 00-1	2744	268	28	n.a.	n.a.	5233	25	29	10.2	98			110		209	180
	34-CA-43	737	56	8	n.a.	n.a.	4650	30	25	13.2	92			25		155	186
	36-CA-46	2379	67	14	n.a.	n.a.	4642	23	27	35.5	170			103		202	172
U65	U65-1	2110	113	52	214	27	4840	22	64	18.7	41	9.9	78.1	96	7.9	220	76
	U-65-12	393	103	37	1374	736	1484	7	104	3.8	11	0.3	0.5	56	1.9	212	14
South Horn Ranger	97-SH-03	1988	154	33	1417	46	4598	23	71	12.9	60	1.4	43.2	86	30.8	200	65
	Ran-3	2025	107	28	n.a.	n.a.	3977	20	52	18.9	72			101		199	76
	Ran-4g	2382	81	18	n.a.	n.a.	4380	29	22	29.4	132			82		151	199

Data are obtained from crush–leach analyses and corrected for the mean Raman chlorinity of the fluid inclusions. n.a.: not analyzed.

Horn. The bulk data confirm the results from individual inclusions: the dominant anion in the analyzed fluids is Cl, and the concentration of SO₄ is low in most samples. The major cations are Na, Ca, Mg, and K; Li is found systematically at lower concentrations confirming the qualitative indications from LIBS. The Na/Ca ratios have values of 0.3 to 10 and the Na/Li ratios have 11 to 240. The Br contents are between 6 and 42 mmol/kg solution (Table 2).

Measurements of $\delta^{18}\text{O}$ in the quartz hosting the brines (Q3), analyzed in collaboration with Geosciences Rennes laboratory (S. Fourcade), yield values between 16 and 18.7‰ (9 data), very similar to those measured at Jabiluka by Polito et al. (2005) for pre-, and post-ore quartz.

5. Origin of the fluids: a discussion based on major cation ratios and trace element data from crush–leach analyses

The Na/K and Na/Li ratios indicate that the analyzed fluid inclusions are similar to sedimentary brines, especially to two types reported in the literature: the highest temperature brines (114–121 °C) from the Mississippi salt dome basin (Kharaka et al., 1987) and some of the brines reported from the Mississippi oil fields (Carpenter et al., 1974). In the Na versus Cl and K versus Cl diagrams (Fig. 8a and b) the data plot above and to the right of the seawater evaporation line according to Fontes and Matray (1993). The concentrations are compatible with seawater that has evaporated past the point of halite and possibly epsomite saturation.

The halogens Cl and Br can be used to distinguish fluid sources (Bohlke and Irwin, 1992), because they

display a conservative behavior in solution and are relatively unaffected by fluid–rock interactions (Banks et al., 1991). The Cl/Br ratios are typical of deep basinal brines. In the Cl/Br versus Cl diagram (Fig. 8d), the brines mainly plot below the seawater evaporation line with Cl/Br ratios typical of fluids which reached saturation with respect to epsomite. The Cl/Br versus Na/Br diagram (Fig. 8c) shows that most data plot around the seawater trend, and could not be obtained by simple halite dissolution. In addition, most Na/Br and Cl/Br ratios (Fig. 8c) are lower than those of seawater, as are most inclusions found in evaporite halite (Horita et al., 1991; Kesler et al., 1996). A contribution of Br from organic matter is unlikely as the continental eolian sandstone contains almost no organic matter, and the basement contains only graphite. The data suggest that the high salinity, Br-enriched fluids were residual brines that result from precipitation of halite from evaporated seawater. However, the salinity of the fluid inclusions is lower than the conservative Cl/Br ratio would require if these were pristine fluids. The lower salinity recorded in the fluid inclusions indicate that the brines have been diluted with another fluid, possibly in the zones where the host-minerals of the inclusions crystallized.

The Na-rich and Ca-rich brines are characterized both by an enrichment in Ca in comparison with seawater or evaporitic brines, and by a depletion in Mg (Fig. 9) which can be attributed to extensive fluid–rock interactions with the basement rocks, e.g. the albitization of Ca-plagioclase (Na-depletion), and the intense chloritization (Mg depletion), which are the two main water–rock interaction products observed of the vicinity of U-ores in the basement (Wilde et al., 1989 and references therein).

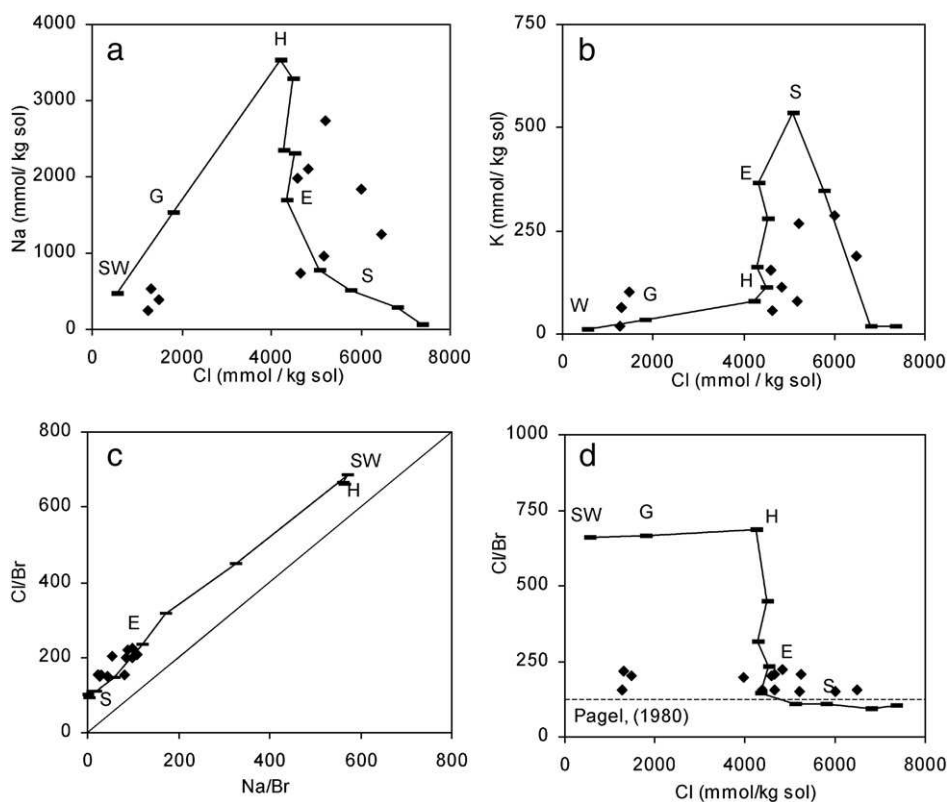


Fig. 8. Na versus Cl (a), K versus Cl (b), Na/Br versus Cl/Br and Cl/Br versus Cl diagrams of the composition of the fluids determined from crush-leach analyses. Full line: sea water evaporation trend from Fontes and Matray (1993). SW: sea water, G: gypsum, H: halite, E: epsomite, S: sylvite.

Na–Ca brines having a residual evaporitic brine component are described in a variety of sedimentary basins and their underlying basement. Most of these Na–Ca brines described in the literature are linked to fluid migrations related with major geodynamic events, and to F–Ba–Pb–Zn deposits, some of which have features typical of the Mississippi Valley Type deposits (Behr et al., 1993, for deep infiltration in basement (KTB deep drilling project, Germany), Heijlen et al., 2001 and references herein (evaporite brines in relation with Zn–Pb ore deposits), Boiron et al., 2002; Cathelineau et al., 2004 for the Mesozoic brine migration within Hettangian formations and its basement in the western part of the French massif central). In most of the examples, Na–Ca or Ca-rich brines have been described mostly on the basis of the eutectic temperatures, and quantitative data on individual inclusions are lacking, the data being mostly from crush and leach analyses (Heijlen et al., 2001; Boiron et al., 2002). In most cases, Na remains the predominant cation although Ca and Mg are major ions in the brines. The origin of the CaCl_2 -rich brine where Ca is by far the dominant cation is difficult to explain. Such brines have

been already described in two other Proterozoic basins (Franceville Basin, Mathieu, 1999; Athabasca basin, Derome et al., 2005). They also occur in Silurian strata

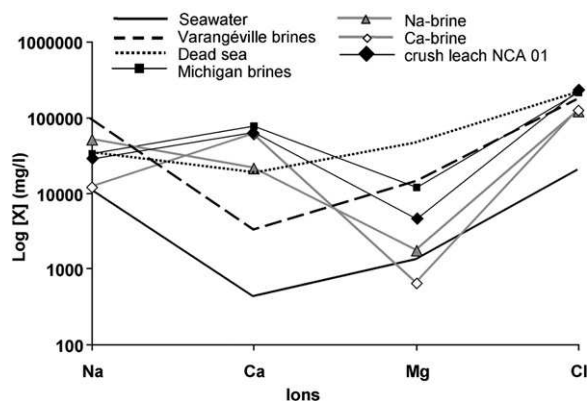


Fig. 9. Main cation concentrations in Na-rich and Ca-rich brines from Caramal (LIBS and Raman data) compared to the bulk fluid composition (crush-leach analysis, sample NCA 01), and reference waters (Seawater (Fontes and Matray, 1993)), evaporite brines (Varangéville, Trias, eastern part of the Paris basin), Dead Sea water, deep basinal brines (Michigan basin, Wilson and Long, (1993)).

from the Michigan Basin (Wilson and Long, 1993; Davisson and Criss, 1996) and have been described from direct sampling and analysis of deep brines in basement rocks in the Canadian shield (Frape and Fritz, 1987) and within the Bohemian basement (KTB, Lodemann et al., 1997). The origin of the Ca-brines is still the object of discussion as two distinct models, one of infiltration of evaporite brines (Behr et al., 1993) and the other of deep formation of brines in relation with geotectonic processes (Lodemann et al., 1997) are proposed, even for the same geological case such as the KTB. Such high calcium contents are generally considered as the result of the interaction between NaCl-rich brines and Ca-rich rocks (Wilson and Long, 1993; Hanor, 1994; Davisson and Criss, 1996). Interaction of NaCl-rich brines with Ca-rich minerals (e.g. albitization of plagioclase, chloritization of pyroxene and amphibole) in the basement lithologies is thus the most likely explanation for the CaCl_2 -rich brines found at Caramal and other localities from Kombolgie basin.

For a mean temperature of 150 °C, the $\delta^{18}\text{O}$ of the fluid that would have been in equilibrium with quartz is between 0.9 and 3.3‰ (most values lie around $1.5 \pm 0.5\text{‰}$), typically within the range of values proposed by Polito et al. (2005) for the U-bearing fluids (0 to 8‰) at Jabiluka. On the basis of the $\delta^{18}\text{O}$ values, these fluids cannot be pristine marine waters. Such isotopic signatures are more typical of fluids equilibrated at low-temperatures (100–150 °C) and at low fluid/rock ratios with sedimentary rocks. Like many examples of basinal brines, the isotopic compositions of the highly saline fluids are most likely the result of several processes, including evaporation (the evaporitic brine component) and mixing (e.g., Knauth and Beeunas, 1986), combined with the interaction of the fluids with ^{18}O -enriched sediments at temperatures of 100 to 150 °C (e.g. Taylor, 1987; Kyser and Kerrich, 1990).

6. Conclusions

The comparison between the independent analytical methods (microthermometry, LIBS, Raman and crush–leach analyses) points out the efficiency of coupling LIBS and Raman spectroscopy to reconstruct the detailed composition of individual fluid inclusions, especially when the inclusions undergo unsuspected metastable phase transitions. When hydrohalite was observed, the bulk composition determined from the ice and hydrate melting temperatures was in good agreement with the Raman and LIBS analyses. However, the Raman microprobe remains indispensable in identifying hydrates and LIBS is recommended to detect other

cations, such as Mg^{2+} , Sr^{2+} , Li^+ , and Ba^{2+} . This is particularly the case for fluid inclusions that have eutectic melting temperatures lower than those of binary systems (H_2O – NaCl ; H_2O – CaCl_2 ...) for which more complex compositions are indicated, involving both Na^+ , Ca^{2+} and probably other cations.

This approach has permitted the identification of three types of fluids that migrated in the Kombolgie Formation in relation with the main fluid activity responsible for the major U-deposits: an Na-rich brine with occasional Mg concentrations, a Ca-rich brine with low Mg concentrations, and a lower salinity fluid. The Ca and Na-brines mixed with each other and also mixed with a less saline end-member. These three fluid-end members and their mixing trends are also observed on a regional scale (Derome et al., 2003) in all the studied localities. A wide range of compositions between the end-members suggest that fluid mixing occurred in the breccia zone itself during periods of fluid influx, as no complete homogenization of the fluids compositions has occurred. These three fluid types are found either in the faulted sandstones or within the faulted basement in relation with U-ores. It can be noted that recent studies claim that U-ore fluids were distinct from those related to the main silicification events affecting the studied faults. At Jabiluka, all fluid types were found in close relation with the ores within the basement. We therefore disagree with conclusions from Polito et al. (2005) who considered quartz Q3 as late and unrelated to U-ore deposition, on the basis of U–Pb discordia ages. As there are no relationships between primary inclusions in quartz, and the quasi-continuous and episodic loss of U from the uraninite lattice, a process observed in most U-ores and which cannot be used for dating fluid events, this indirect dating of fluids has no chronological or textural support.

The brines are enriched in Br, and are interpreted as residual brines probably linked to the evaporite layers which are found in the McArthur basin. Brines evolved chemically during their interaction with the Proterozoic basement and the mid-Proterozoic siliciclastic sediments, as the Ca concentrations are likely the result of interaction of the Na-brine and Ca-rich lithologies. The Ca-enrichment probably occurred when the fluid migrated from shallow levels in the basin down to the contact with the basement along and below the unconformity. Thus, the breccia bodies at the base of the Kombolgie sandstone represent active drainage zones where different fluid reservoirs were connected, and thus a place where fluid mixing was highly favored. These fluid movements are considered as related to the main processes responsible for the U-mineralization at the unconformity or below.

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