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Percolation of diagenetic fluids in the Archaean basement of the Franceville basin

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A B S T R A C T

The Palaeoproterozoic Franceville basin, Gabon, is mainly known for its high-grade uranium deposits, which are the only ones known to act as natural nuclear fission reactors. Previous work in the Kiéné region investigated the nature of the fluids responsible for these natural nuclear reactors. The present work focuses on the top of the Archaean granitic basement, specifically, to identify and date the successive alteration events that affected this basement just below the unconformity separating it from the Palaeoproterozoic basin. Core from four drill holes crosscutting the basin–basement unconformity have been studied. Dating is based on U–Pb isotopic analyses performed on monazite. The origin of fluids is discussed from the study of fluid inclusion planes (FIP) in quartz from basement granitoids. From the deepest part of the drill holes to the unconformable boundary with the basin, propylitic alteration assemblages are progressively replaced by illite and locally by a phengite + Fe chlorite ± Fe oxide assemblage. Illitic alteration is particularly strong along the sediment–granitoid contact and is associated with quartz dissolution. It was followed by calcite and anhydrite precipitation as fracture fillings. U–Pb isotopic dating outlines three successive events: a 3.0–2.9-Ga primary magmatic event, a 2.6-Ga propylitic alteration and a late 1.9-Ga diagenetic event. Fluid inclusion microthermometry suggests the circulation of three types of fluids: (1) a Na–Ca-rich diagenetic brine, (2) a moderately saline (diagenetic + meteoric) fluid, and (3) a low-salinity fluid of probable meteoric origin. These fluids are similar to those previously identified within the overlying sedimentary rocks of the Franceville basin. Overall, the data collected in this study show that the Proterozoic–Archaean unconformity has operated as a major flow corridor for fluids circulation, around 1.9 Ga.

1. Introduction

The Archaean granitoids of the Kiéné area, Gabon, are covered with Palaeoproterozoic sediments from the Franceville basin deposited at about 2.1 Ga. This basin contains natural nuclear fission reactors, which occur in the Oklo, Bangombé and Okélobondo deposits. It also hosts the Moanda Mn deposit, the second largest reserve of manganese in the world.

Former studies of Precambrian basements at the unconformity below sedimentary basins generally show three successive alteration events: (1) metamorphism, (2) palaeoweathering, and (3) diagenetic fluid/basement interaction (Murakami et al., 2011; Nedachi et al., 2005; Panahi et al., 2000; Rainbird et al., 1990). Evidence for diagenetic fluid/basement interaction has been provided

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by mineralogical observations and major and trace element chemical analyses. This interaction essentially corresponds to pervasive illite crystallization at the unconformity level associated with K enrichment (Nedachi et al., 2005; Panahi et al., 2000).

A scientific problem that has not been addressed so far in the Franceville basin is the physicochemical and chronological characterization of basinal fluids that have reacted with the basement. Previous fluid inclusion studies of the Franceville basin have been limited to the sedimentary formations (Gauthier-Lafaye, 1986; Mathieu et al., 2000; Michaud and Mathieu, 1998). These authors have identified several fluids related to the formation of diagenetic minerals in the basin, the generation of U ore deposits, and the migration of hydrocarbon-rich fluids. These fluids are:

(1) highly saline diagenetic brines;
(2) hydrocarbon-rich fluids derived from organic matter-rich formations;
(3) a low-salinity fluid likely of meteoric origin migrating through the granitic basement;
(4) mineralizing fluids resulting from the mixing of fluids 1 and 3;
(5) high-temperature fluids resulting from the natural nuclear reactor environment (Mathieu et al., 2000).

The present paper attempts to characterize the succession of alteration events that have affected the top of the basement below the Palaeoproterozoic sediment unconformity. Are these alterations related to early post-magmatic to hydrothermal events, to palaeoweathering, or to late infiltration of diagenetic brines from the overlying basin? Our study, carried out on drill core samples from Kiéné, is supported by petrographic investigation, new fluid inclusion data and U–Pb geochronology on monazite.

2. Geological setting

2.1. Basement

The basement of the Franceville basin, located in southeastern Gabon, is mainly composed of Archaean TTG, gneiss and granitoids (Bouton et al., 2009; Caen-Vachette et al., 1988). The granitic rocks were emplaced during two main events (Bouton et al., 2009; Chevallier et al., 2002; Prian and Johan, 1989; Thiéblemont et al., 2009); the first one occurred during the Mesoarchaean (2928 ± 6 Ma to 2870 ± 5 Ma) and produced calc-alkaline granitoids, generally of grey colour with characteristics similar to those of the Archaean TTG series (Trondjemite, Tonalite, Granodiorite) and quartz-diorites with migmatic facies (Thiéblemont et al., 2009). They are locally crosscut by basic dykes (diorite). The second plutonic event occurred during the Neoarchaean (2800 to 2550 Ma) and produced alkaline to calc-alkaline pink and red magmatic rocks: syenites, syenogranites to granites, and pegmatites (Thiéblemont et al., 2009).

2.2. The Franceville Basin

Overlying the Archaean basement, the 2000-m thick Franceville sedimentary basin (Ossa Ossa et al., 2013) is comprised of five unmetamorphosed sedimentary and volcano-sedimentary sequences. From bottom to top, these are (Weber, 1968; Weber and Gauthier-Lafaye, 2013):

- the FA formation (500–1000 m thick), directly deposited on the Archaean granitoids, consists of red, green and black sandstones and conglomerates (Gauthier-Lafaye and Weber, 1989);
- the FB formation (400 to 700 m thick), dominated by black shale with interbedded breccia and sandstone of turbiditic origin (Azzibrouck-Azzilez, 1986; Mossman et al., 2005; Parize et al., 2013; Thiéblemont et al., 2009);
- the FC, FD and FE formations (less than 300 m), mainly composed of stromatolitic chert, black shale and sandstone, respectively (Bertrand-Sarfati and Potin, 1994; Préat et al., 2011).

The diagenetic event resulted in a silicification of the detrital quartz grains and the formation of authigenic illite and chlorite in the matrix (Gauthier-Lafaye, 1986; Gauthier-Lafaye and Weber, 1989).

3. Sampling and analytical procedures

All data were obtained on four drill holes (GR1, GR20, GR23 and KA6) from the central part of the Franceville Basin, in the Kiéné region, previously prospected by Haubensack (1981). The granitoids were sampled from the FA-basement contact to a maximum depth of 15 m into the Archaean basement. The petrographic investigation mainly focused on the alteration features and mineralogy of secondary phases. Samples were selected according to the distance from the unconformity and to the different alteration types affecting the basement (Table 1). Samples GR20 833, GR23 640.5, GR23 631.5 are located at 10.75, 14 and 2.25 m below the unconformity, respectively. Samples

Table 1
Recapitulative results of microthermometry performed on quartz FIP.

Depth (m) below unconformity	Sample name	Host rock	$T_{m\ ice}$ (°C)	T_h (°C)	Number of analyses	Alteration type
Base of sedimentary formation	KA6 436	Sandstone	−7.9 to −0.1	204.4 to 127	10	Illite (+ phengite) in matrix
0	GR20 819	Tonalite	−23 to −0.2	101.7 to 223	9	Illite (+ hematite + phengite) in matrix
0.85	KA6 437.85	Tonalite	−19.7 to −0.1	166.6 to 127	9	Illite (+ phengite) in matrix
2.75	GR23 631	Tonalite	−28.2 to −0.4	160.9 to 97	5	Chlorite (+ calcite + anhydrite) in fracture
10.75	GR23 640	Tonalite	−39.6 to −1.2	191.2 to 95.7	13	Chlorite (+ epidote + calcite) in fracture
14	GR20 833	Gneiss dioritic	−33.7 to −1.3	169.4 to 96	15	Chlorite (+ epidote + anhydrite + calcite)

GR20 819, GR1 631 and KA6 437.85 are located less than 2 m below the unconformity. KA6 436 is located at the base of the FA sandstone. The dating was obtained by U–Pb isotopic analysis on monazite from samples KA6 437.85 and GR1 631. These are located at 0.85 and 1.00 m, respectively, below the FA sandstone–basement interface.

Microthermometry was carried out on fluid inclusions from selected fluid inclusion planes (FIP) in quartz using a Linkam MDS600 heating-cooling stage adapted to an Olympus optical microscope. These analyses were performed at the GeoRessources laboratory, Université de Lorraine. Accuracy at low temperatures ($T < 20\,°C$) is 0.1 °C, through calibration checks every week and occasional checks during these intervals. Calibration at high temperature ($T > 100\,°C$) is performed by standard solid melting (Roedder, 1984) and the use of synthetic fluid inclusions. The uncertainty for high temperatures is ± 2 °C, or more (± 5 °C) for very high temperatures (≥ 400 °C).

The dating was obtained by U–Pb isotopic analysis on monazite crystals, whose properties as traps for fissiogenic elements were highlighted by Montel (2011). These crystals were examined using SEM, mostly in backscattered electron mode, and using an electron microprobe (Cameca SX50) at the CAMPARIS centre (University Pierre-et-Marie-Curie, Paris-6). U–Pb isotopic data were obtained by laser ablation coupled with a mass spectrometer (LA–ICPMS) at the Volcanology Laboratory of Clermont-Ferrand University. These analyses involved ablation of minerals with a Resonetics Resolution M-50 powered by an ultrashort-pulse (< 4 ns) ATL Atlex Excimer Laser system operating at a wavelength of 193 nm (Muller et al., 2009). A 7-μm laser spot diameter and a repetition rate of 1 Hz with an 8-mJ energy, producing a fluence of 15 J/cm^2 were used.

4. Results

4.1. Petrography and alteration

The least altered granitoids are grey or pink-to-red coloured. They are tonalite, granodiorite, and granite. The primary minerals are quartz, plagioclase, biotite, alkali feldspar, and locally amphibole. Zircon, apatite, uranothorite and monazite are the common accessory mineral phases. Locally, the grey granitoids present a gneissic structure.

Table 2
Representative chlorite microprobe data and structural formulae calculated on the 14 oxygen basis.

	Microprobe analyses				Stuctural formulae		
SiO_2	28.79	29.01	27.19	Si	2.91	2.99	3.05
TiO_2	0.21	0.15	0.03	AlIV	1.09	1.01	0.95
Al_2O_3	19.63	19.05	16.31	AlVI	1.26	1.31	1.21
FeO_t	22.95	25.95	13.89	Ti	0.02	0.01	0.00
MnO	0.74	0.20	0.20	Fe2+	1.94	2.24	1.30
MgO	17.33	14.55	19.78	Mg	2.61	2.24	3.31
CaO	0.05	0.03	0.02	Mn	0.06	0.02	0.02
Na_2O	0.00	0.02	0.02	Ca	0.01	0.00	0.00
K_2O	0.04	0.26	0.08	Na	0.00	0.00	0.00
Total	89.74	89.22	77.50	K	0.01	0.03	0.01

The granitic basement is affected by strong alteration that shows a well-developed zoning from the base of studied drill core in the granitoids (15-m depth) to the FA-granitoid unconformity. At the bottom of the drill holes, the granitoids are affected by an early propylitic alteration. The uppermost part of the granitoidic basement is largely affected by an illitic alteration. Here, the alteration imparts a green or red colour to the rock.

The propylitic alteration is characterized by pervasive crystallization of Mg-chlorite, epidote, allanite, calcite, and titanite. Chlorite and epidote have also precipitated in fissures. Locally, late calcite replaces feldspar or occurs along cracks in association with chlorite. The temperature domain of the propylitic alteration, and associated chlorite–epidote paragenesis, has been estimated using the chlorite geothermometer of Cathelineau (1988) in the 250–300 °C. The microprobe data are presented in Table 2.

The illitic alteration is mainly pervasive and characterized by an illite–phengite–haematite assemblage associated with corrosion of quartz crystals in the sandstone above the unconformity and in the plutonic rocks of the basement (Fig. 1). Illite crystallized as plagioclase replacement, whereas phengite and haematite replaced previously chloritized biotite. The illitic alteration has affected the granitic basement pervasively 4 to 5 m below the unconformity and locally extends down to a depth of 7 m along fractures. Late-stage carbonates, locally associated with anhydrite, occur in microfractures that crosscut illitized rocks.

Illitic alteration is also observed in FA sandstone above the unconformity and in FB black shale. The illitic matrix

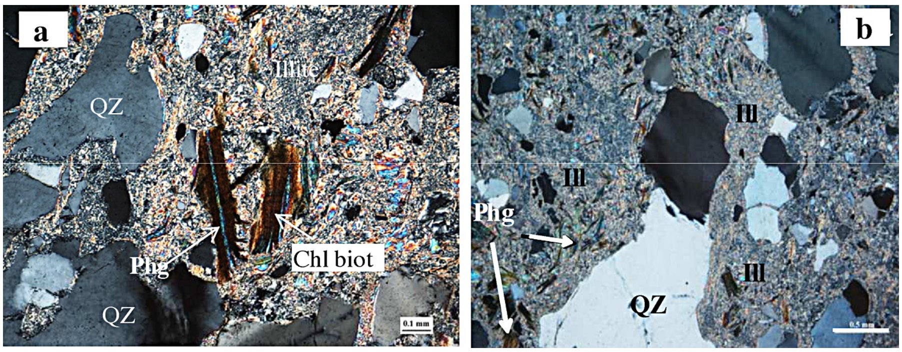

Fig. 1. (Color online). Photomicrographs of illitized granitoid, (a) chloritized biotites (Chl biot) replacement by two phengites (Phg), (b) quartz presents evidence of strong corrosion.

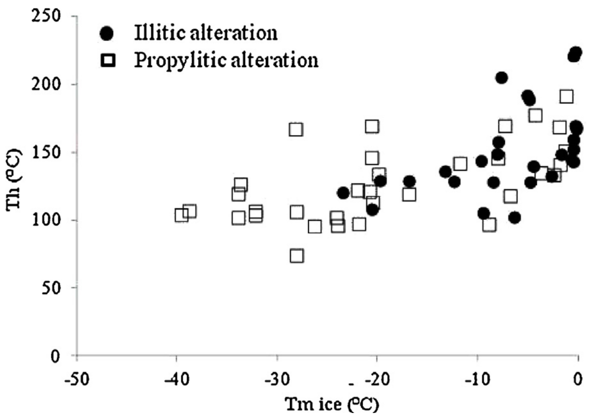

Fig. 2. Homogenization temperature (T_h) vs ice-melting temperature ($T_{m\ ice}$) diagram for fluid inclusions analysed in quartz in illitized FA sandstone, illitized, and propylitized granitoids.

has filled all intergranular porosity and has replaced the feldspars. Illite in FA sandstones is associated with calcite, anhydrite and barite.

4.2. Fluid inclusion microthermometry

Fluid inclusions have been studied in primary quartz of plutonic rocks from the basement and in primary detrital quartz of one sandstone sample. All inclusions show generally two phases (an aqueous liquid and a vapour phase representing 5 to 10 vol. % of the inclusion volume). Three-phase inclusions (liquid + vapour + salt) and single-phase inclusions (liquid phase only) were rarely observed. The fluid inclusions from the propylitized samples show sizes up to 20 μm, whereas those from the illitized samples close to the unconformity and from the base of the FA sandstone have smaller sizes (5–10 μm). The two-phase fluid inclusions of propylitized samples are characterized by a wide range of ice-melting temperatures ($-39 < T_{m\ ice} < -0.1$ °C) and homogenization temperatures ($95 < T_h < 206$ °C; Fig. 2 and Table 1). The fluid inclusions of the illitized samples close to the unconformity and from the base of the FA sandstone are characterized by a large range of ice melting temperatures ($-23 < T_{m\ ice} < -0.1$ °C) and homogenization temperatures ($132 < T_h < 220$ °C; Fig. 2 and Table 1). The highest salinity fluids have not been observed in this alteration zone.

The fluid inclusions with the highest salinity (i.e., the lowest $T_{m\ ice}$) tend to show the lowest homogenization temperature (Fig. 2). The same trend was also observed for the fluids from the Franceville Basin (Openshaw et al., 1978; Mathieu, 1999; Mathieu et al., 2000), the Athabasca Basin (Canada) (Boiron et al., 2010), the Kombolgie Basin (Australia) (Boiron et al., 2010) and in the basement below an unconformity in the northwestern part of the French Massif Central (France) and at Soultz (France) (Boiron et al., 2010; Cathelineau & Boiron, 2010).

4.3. Geochronological data

Monazite crystals were analysed from samples KA6 437.85 (0.85 m below the unconformity) strongly illitized and GR1 631 (1 m below the unconformity) less illitized. In the GRI 631 sample, some feldspars are replaced by calcite and illite, and most of microcracks, filled by calcite and locally quartz, crosscut the illitized feldspars. In sample KA6 437.85, monazite occurs as euhedral, elongated, millimeter-size crystals scattered in the illitic matrix with no evidence of alteration. In sample GR1 631, the monazite crystals are xenomorphic, often grouped in aggregates, and they are locally associated with pyrite, illite and uranothorite.

The monazites from these two altered samples are characterized by low Th contents ($ThO_2 < 1.4$ wt%) compared to the detrital monazites from the FA sandstones (average $ThO_2 = 4$ wt%) described by Mathieu et al. (2000). The euhedral monazite crystals of the illitized sample (KA6 437.85) are richer in Th (up to 1.4 wt %) and poorer in U ($23 < U < 138$ ppm) than those of the sample GR1 631 with the illite–carbonate alteration ($25 < Th < 2263$ ppm and $199 < U < 466$ ppm). Plotted in the $^{206}Pb/^{238}U$ versus $^{207}Pb/^{235}U$ diagram, the U–Pb isotopic data of euhedral monazite from sample KA6 437.85 give two groups of discordia ages (Fig. 3a): from 2998 ± 25Ma (MSWD = 0.72) to 2922 ± 24 Ma (MSWD = 1.4) and 2621 ± 30 Ma

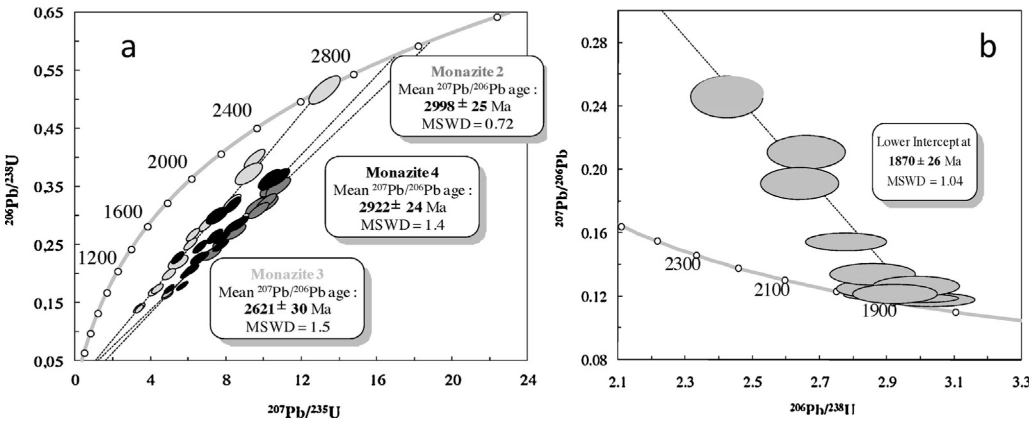

Fig. 3. a: $^{206}Pb/^{238}U$ versus $^{206}Pb/^{238}U$ diagram. Monazites of KA6 437 sample; b: $^{207}Pb/^{206}Pb$ versus $^{206}Pb/^{238}U$ diagram. Monazites of GR1 631 sample. MSWD = mean square weighted deviation.

(MSWD = 1.5). The isotopic data from xenomorphic monazite from sample GR1 631 are plotted in a $^{207}Pb/^{206}Pb$ versus $^{206}Pb/^{238}U$ Tera–Wasserburg diagram because of their high common Pb contents. An age of 1870 ± 26Ma (MSWD = 1.04) is obtained (Fig. 3b).

5. Discussion and conclusion

5.1. Geochronology and alterations

From the deepest part of the bore holes to the unconformity, three successive alteration parageneses are observed, i.e.:

(i) an early propylitic alteration characterized by Mg-chlorite–epidote ± titanite ± allanite paragenesis disseminated in the rock and by carbonate + chlorite crystallization infilling of veinlets;
(ii) a diagenetic alteration characterized by a pervasive illitization, haematite crystallization and quartz dissolution;
(iii) a late diagenetic alteration characterized by calcite ± anhydrite vein filling crosscutting illitized granitoids.

Petrographic observations show the superimposition of the illitic alteration on the propylitic one and the increasing intensity of the illitization toward the unconformity.

The two sets of monazite ages at 2998–2922 ± 25 Ma and 2621 ± 30 Ma in the pervasively illitized sample close to the unconformity are similar to ages of emplacement of the plutonic rocks in the basement (Bouton et al., 2009; Caen-Vachette et al., 1988). The illitic alteration has not modified the isotopic system of monazite. The monazite of the sample GR1 631 affected both illitization and carbonatation gives a younger age of 1870 ± 26 Ma. This age is similar to those reported by Bonhomme et al. (1982), who have dated the thin illitic fraction (0.2 and 0.4 μm) by the Rb–Sr method. These results suggest that the diagenetic fluids responsible for the carbonatation have percolated the basement and have favoured the precipitation of late poor Th and rich U monazite. No age between 2.5 and 2.1 Ga (age of the Franceville Basin), which could be related to a possible palaeoweathering episode, has been recorded.

5.2. Palaeofluid origins

The fluid inclusions measured in the different primary quartz crystals of the granitoids from the unconformity to 15 m downwards into the basement display a wide range of $T_{m\ ice}$ values, from very low to high salinities. These data are similar to those previously obtained on the fluids identified in the different generations of quartz from the Franceville Basin (Gauthier-Lafaye, 1986; Gauthier-Lafaye & Weber, 1989; Mathieu, 1999; Mathieu et al., 2000; Openshaw et al., 1978). The high salinity diagenetic fluids characterized by $-60 < T_{m\ ice} < -46$ °C are Ca-dominated with a Na/Ca ratio around 0.5, and the $-36 < T_{m\ ice} < -27$ fluids are Na-dominated, with a Na/Ca ratio from 2 to 9 (Mathieu et al., 2000). The fluids with $T_{m\ ice} < -21$ °C contain divalent cations, such as Ca^{2+} and or Mg^{2+}, besides Na^{+} (Yanatieva, 1946; Oakes et al., 1990) and the ones with $T_{m\ ice}$ from –15 to–21 °C, referring to the Athabasca Basin, suggest a higher Na/Ca ratio (Mercadier et al., 2010).

The identification in the quartz crystals of the altered plutonic rocks below the unconformity of highly saline and moderate-temperature (130–180 °C) fluids with characteristics similar to those of the diagenetic brines from the Franceville Basin demonstrates that these brines have massively percolated into the basement at least down to –15 m below the unconformity. Similar interaction has been already observed in various localities, such as in the Rhine Graben (France) and below the Athabasca Basin (Saskatchewan, Canada), where brines penetrated the basement down to more than 5 km and 250 m below the unconformity, respectively (Cathelineau and Boiron, 2010; Mercadier et al., 2010; Pagel and Jaffrezic, 1977). The trend defined by $T_{m\ ice}/T_h$ pairs (Fig. 2) could indicate a mixing between diagenetic brine and a low-saline meteoric fluid (Boiron et al., 2010). Such trend has been also described in many basins: southern Norway (Munz et al., 1995, Oliver et al., 2006), Spain (Bouch et al., 2006), France, northwestern Massif Central (Munoz et al., 1999), Athabasca (Mercadier et al., 2010; Richard et al., 2013).

Even if the high- and low-salinity fluids have been identified in the deepest samples, the low-salinity/high-temperature fluids and mixing fluids are predominantly identified in the highly illitized and dequartzified rocks located on each side of the unconformity, i.e., in the FA sandstone and shallow samples from the basement. These results suggest that the fluids with higher temperature and low salinity, of possible meteoric origin according to Mathieu et al. (2000), may be responsible for quartz dissolution and illitization. Their percolation seems to have been more intense at the unconformity and partly erased the highly saline diagenetic fluids, as the latter fluids are rare in the samples located within the few metres either side of the unconformity. On the contrary, in the deepest rocks, the brines trapped in quartz FIP have the highest salinities in samples 15 m below the unconformity, with no evidence of illitization. That argues in favour of the dominant role of the unconformity on the Na–Ca diagenetic fluid circulations between 2.1 and 1.9 Ga. In the basement rocks of the Athabasca Basin, brines having the highest salinity are only observed in the most altered samples (Mercadier et al., 2010). These authors explained the presence of these brines by:

(i) the result of an important gain in Cl during alteration of the biotite into chlorite and illite during the brine stage;
(ii) an important water loss during the alteration of the basement rocks, as demonstrated by the important difference between loss on ignition (LOI) for fresh and altered rocks (1% to 10%).

In the basement of the Franceville Basin, the high salinity of diagenetic fluids observed at 15 m depth may be explained by a similar fluid/rock interaction. On the contrary, the low salinity of fluids observed in the most altered rocks that are located along the unconformity is explained by the massive infiltration of meteoric fluids that mix with the diagenetic brines. The haematite precipitation coexisting with the illitic alteration invading along the unconformity testifies the oxidative conditions that may be associated with the diagenetic and/or meteoric fluids. On the other hand, the petrographic features of the altered basement below the unconformity and dating do not give any argument in favour of an Archaean weathering event between 2.5 and 2.1 Ga.

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