



Hydrothermal clay mineral formation in the uraniferous Paleoproterozoic FA Formation, Francevillian basin, Gabon

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ARTICLE INFO

Article history:

Received 11 December 2013

Received in revised form 27 February 2014

Accepted 6 March 2014

Available online 15 March 2014

Keywords:

Clay minerals

Hydrothermal activity

Oxidized fluids

Relatively high temperature

U mineralization

Francevillian basin

ABSTRACT

The spatial distribution of neoformed clay minerals was investigated in the Paleoproterozoic FA Formation of the Francevillian basin, south-east Gabon, which hosts high-grade U ore deposits associated with the only known occurrence of natural nuclear reactors. Illite appears as the main clay phase in the lower fluvial unit. In the mineralized upper fluvio-deltaic-tidal unit, the clay assemblage is more diversified and commonly characterized by illite, chamosite, berthierine and chamosite/berthierine mixed layers, usually in association with alteration products of U-bearing minerals. The clay mineral assemblage thus potentially constitutes a mineralogical marker for the regional distribution of U ore deposits.

Polytype species of the clay phases indicate mineral transformations in an environment characterized by a high fluid/rock ratio. According to crystalline structure, mineral chemistry, thermodynamic modeling and geochronology, clay phases seem to be mainly hygrothermometer, rather than exclusively a thermometer, and their formation, as well as associated dissolution-precipitation of U-bearing minerals took place between ca. 2040 and 2010 Ma ago, at temperatures of about $240 \pm 30^\circ\text{C}$. Using previous burial estimates, this suggests the operation of hydrothermal processes controlled by an external heat source, likely associated with volcanism during deposition of the FD and FE formations. Hydrothermal activity, involving oxidized fluids, would have driven U remobilization and, ultimately, formation of high-grade U ore deposits. The thermal history proposed here allows for a better understanding of the conditions during burial of the sedimentary succession and the origin of its rich U endowment.

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1. Introduction

Most studies of the Franceville sub-basin have focused on its western part near the famous nuclear fission reactors (Cortial et al., 1990; Cuney and Mathieu, 2000; Gauthier-Lafaye, 2006; Gauthier-Lafaye et al., 1989, 1996; Gauthier-Lafaye and Weber, 1989; Hidaka and Gauthier-Lafaye, 2000; Mathieu et al., 2000, 2001), while few investigations have been carried out at the regional scale. In the Franceville sub-basin, five formations (from FA at the bottom to FE at the top) have been described (Gauthier-Lafaye, 2006; Gauthier-Lafaye and Weber, 1989, 2003; Weber, 1968). Despite the uniquely low metamorphic grade of this sedimentary succession (Cortial

et al., 1990; Gauthier-Lafaye and Weber, 1989; Mathieu et al., 2000; Ossa Ossa et al., 2013), the stratigraphic subdivision of the basin fill remains poorly understood at the regional scale due to extensive normal faulting and poor exposure (Azzibrouck-Azzile, 1986; Gauthier-Lafaye and Weber, 1989; Pambo et al., 2006; Pr  at et al., 2011; Thi  blemont et al., 2009; Weber, 1968). A better understanding of the basin architecture and burial history would improve exploration of sediment-hosted ore deposits (e.g. U, Mn) present in this sedimentary basin.

On the basis of fluid inclusion studies of quartz cement, Openshaw et al. (1978, reviewed by Gauthier-Lafaye and Weber, 1989), provided estimates of the temperatures during diagenetic quartz cementation of FA sandstones close to the nuclear reactor zones. Two different geothermometers gave values of ca. 238 and 183°C . Using the latter value with a corresponding fluid pressure of 410 bar, a geothermal gradient of $40^\circ\text{C}/100$ bars and a maximum burial of 4100 m was estimated for the upper part of the FA Formation, assuming that the fluids were in the hydrostatic

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pressure regime (Gauthier-Lafaye and Weber, 1989; Mathieu et al., 2000). The diagenetic history of the basin is crucially important, as U mineralization is generally ascribed to leaching of U-bearing detrital accessory minerals (mainly monazite and zircon) by diagenetic brines during the burial phase, followed by precipitation along the FA/FB redox-boundary, the absolute timing of which is not well known (Cortial et al., 1990; Gauthier-Lafaye and Weber, 1989; Mathieu et al., 2000). The parameters controlling diagenetic mineral transformation, leaching and remobilization of U and the thermal history of the sedimentary succession are also poorly constrained. As a result, the conditions under which leaching, mobilization, and precipitation of U occurred require further investigations.

Neoformed clay minerals can be used to evaluate the nature and evolution of the thermal history of sedimentary basins in general (Meunier, 2005), and the spatial distribution of alteration halos in sedimentary rocks hosting U ore deposits in particular (Beaufort et al., 2005; Kister et al., 2006; Laverret et al., 2006). In this study, we will focus on the composition of clay minerals observed in the FA Formation (see SI text; Coombs et al., 2000; Damyanov and Vassileva, 2001; Foster, 1962; Gottesmann and Förster, 2004; Iijima and Matsumoto, 1982; MacKenzie and Berezowski, 1984; Pezzotta et al., 1999; Slack et al., 1992; Wise, 2007; Yau et al., 1988). The main objective of this paper is to highlight the spatial distribution of clay mineral assemblages and associated dissolution-precipitation processes of U-bearing minerals at the scale of the Franceville sub-basin. The goals are to establish: (1) potential mineralogical markers allowing for a better understanding of the regional distribution of sedimentary units hosting U ore deposits, (2) the age of clay minerals to test the hypothesis that they are coeval with U mineralization and volcanic activity, (3) parameters under which U mobilization and precipitation occurred, and (4) how clay minerals could be helpful for a better characterization of the regional fluid flow related to U migration.

2. Geological setting

The Franceville sub-basin is one of four major sub-basins of the Paleoproterozoic Francevillian Basin in southeastern Gabon (Fig. 1). It is characterized by an essentially unmetamorphosed fluvial to shallow-marine sedimentary succession dated at ca. 2.1 Ga (Bonhomme et al., 1982; Bros et al., 1992). The basin fill has been divided lithostratigraphically into five formations (Fig. 2) from FA at the bottom to FE at the top (Gauthier-Lafaye and Weber, 1989, 2003; Weber, 1968). The FA Formation is characterized by two main sedimentary units, a sandstone-dominated fluvial succession and an overlying fluvio-deltaic-tidal succession of sandstones and shales (Fig. 2). The FB Formation consists predominantly of black shales that are locally enriched in Mn, forming the protore for important supergene Mn deposits. The FA/FB contact is represented by a transition from fluvial to fluvio-deltaic to open-marine depositional settings.

The geodynamic history of the basin can be divided into three major tectonic phases of unequal duration (Gauthier-Lafaye and Weber, 1989, 2003). Intracratonic extension during the first phase led to a basin where maximum subsidence was confined to areas adjacent to NW-SE and N-S trending faults, giving rise to deposition of the FA Formation. The second phase is characterized by rapid subsidence in NW-SE and N-S trending grabens and the deposition of fine-grained clastic and chemical sedimentary rocks (FB and FC formations). The last tectonic phase was dominated by an expansion of the subsidence area across the entire Francevillian Basin, resulting in deposition of the predominantly siliciclastic sediments of the FD and FE formations in association with major acidic volcanism (Gauthier-Lafaye and Weber, 1989, 2003).

3. Materials and methods

3.1. Sampling

Sampling of the FA Formation was undertaken in different parts of the Franceville sub-basin, from areas close to and far away from natural nuclear reactors (Fig. 1). The study is based on 30 selected samples on which petrographic, XRD, and thermodynamic investigations were undertaken systematically. These investigations were coupled with geochronological analysis. The samples are representative of all FA facies and were obtained from three selected areas (Figs. 1 and 2): (1) Mounana (edge of basin), near the Oklo reactors; (2) Moanda (edge of basin), near the Bangombe reactor; (3) Mikouloungou-Kiééné-Otobo (central part of the basin), about 30 km away from any known reactor.

3.2. Petrography and electron microscopy

Petrographic and textural analyses were done on (1) polished thin-sections using a Nikon ECLIPSE E600 POL polarizing optical microscope; (2) carbon-coated polished thin sections using a JEOL JSM6400 scanning electron microscope (SEM) operating at 15 keV and 1 nA, equipped with an electron back-scattering detector and an energy dispersive spectrometer (EDS) using a liquid nitrogen-cooled Si(Li) semi-detector at the University of Poitiers. The EDS calibration standards were albite, forsterite, orthoclase, wollastonite, manganese metal, titanium metal and pyrite.

X-ray compositional maps of monazite were obtained from carbon-coated polished thin sections using a four spectrometer-equipped Cameca SX-100 electron microprobe (EMP) at SPEC-TRUM, University of Johannesburg. Operating conditions were 15 kV acceleration, 40 nA beam current, and 500 ms dwell time per spot. Cesium ($L\alpha$), Nd ($L\beta$), U ($M\beta$) and Y ($L\alpha$) were analyzed by wavelength dispersion spectroscopy (WDS). Calcium ($K\alpha$), P ($K\alpha$), Si ($K\alpha$), Th ($M\alpha$), La ($L\alpha$) and Pb ($L\alpha$) were analyzed by EDS. Maps are up to 250×250 pixels in size, with 1.5–2 μm step (distance between analysis spots, or spatial definition), and show uncalibrated (semi-quantitative) element distributions (as total counts, cts). EMP spot analyses of chlorite (approximately 150 analyses) were carried out on the same instrument as the X-ray maps, with the following analytical settings: 15 kV acceleration, 20 nA beam current, 5 μm spot size, 1.5 min total counting time. Almandine (Al), hematite (Fe), orthoclase (K), jade (Na), olivine (Mg), apatite (P), wollastonite (Ca), rutile (Ti) and diopside (Si) have been used as standard materials.

3.3. X-ray diffraction and clay minerals

XRD patterns were recorded using a Panalytical Xpert Pro diffractometer with $\text{CuK}\alpha$ radiation (40 kV, 40 mA) equipped with a stepping-motor drive on the goniometer at University of Poitiers. The diffracted beam was measured with an X'celerator detector. Clay mineral characterization was performed on air-dried and glycolated oriented preparations (on $<2 \mu\text{m}$ fraction and magnetic fraction from 4° to $30^\circ 2\theta$), and powders ($<2 \mu\text{m}$ magnetic fraction) for main (hkl) reflections of chlorite and berthierine (from 30° to $65^\circ 2\theta$). The NEWMOD program of Reynolds (1985) was used to simulate XRD diffractograms to identify and quantify the components within the mixed layer clay minerals.

Fe-chlorite, including Chm and Bert of the clay fraction were collected by magnetic separation. Separation was performed using a Varian 3603 (University of Poitiers), whose pole pieces are 10 cm in diameter with a gap of 4 cm, and where a uniform magnetic field adjustable up to 2 Tesla can be applied. The used device is placed

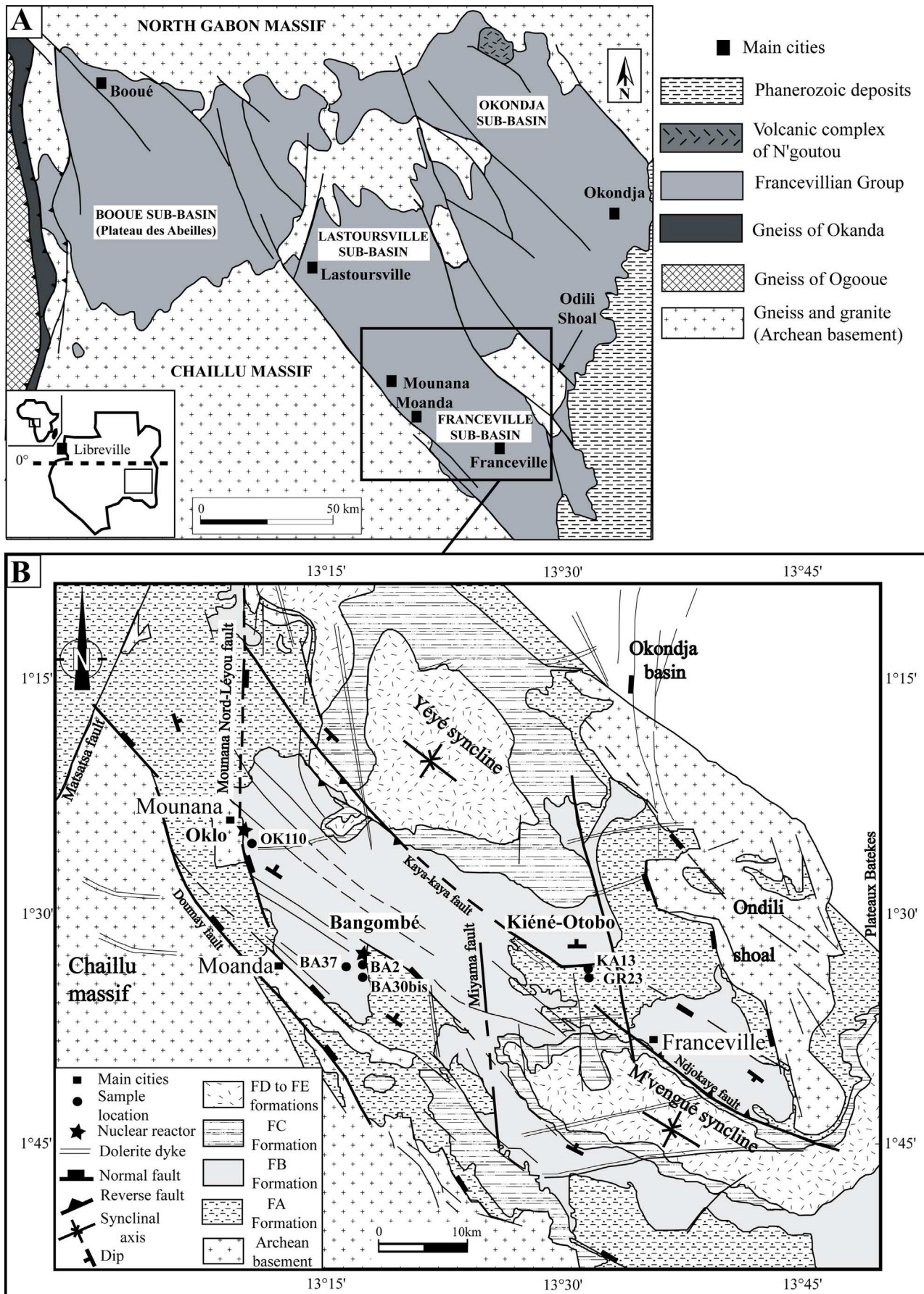


Fig. 1. Geological map of the Francevillien Basin (A) and Francevillien sub-basin (B) showing sample locations (modified after Gauthier-Lafaye and Weber, 2003; Pambo et al., 2006).

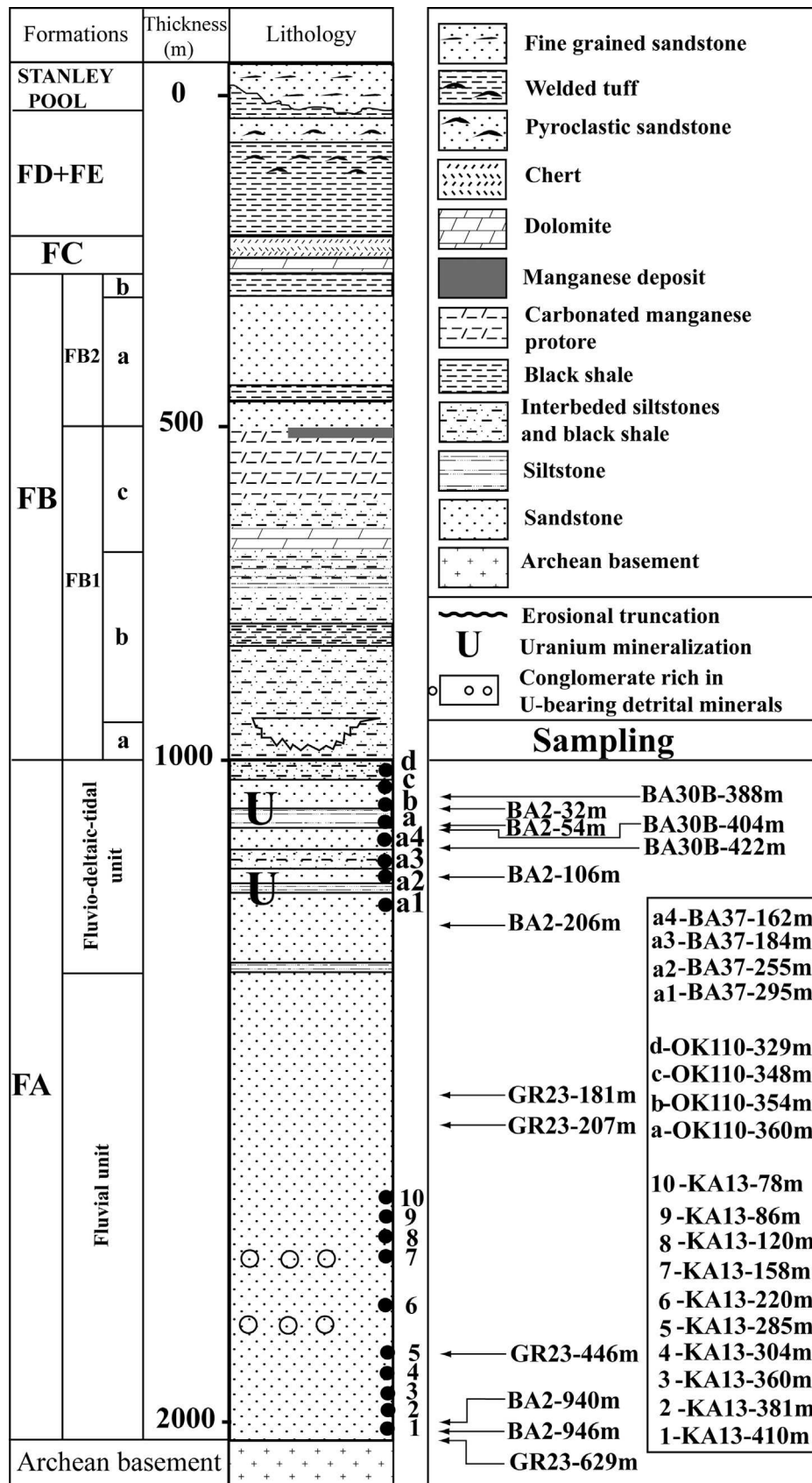


Fig. 2. Lithostratigraphic column of the Francevillian Group and sampling sites (modified after Gauthier-Lafaye and Weber, 2003).

in the gap of the electromagnet and consists of a peristaltic pump in which the suspension circulates in a closed circuit in a plexiglas cell containing a steel wire grid.

3.4. Geochronology: $^{40}\text{Ar}/^{39}\text{Ar}$ dating

About 2 mg of a <2 μm fraction of pure illite from sample BA2-946 m (see Figs. 1 and 2) was irradiated at NTP radioisotopes SAFARI1 nuclear reactor at Pelindaba, South Africa, in position B2W for 20 h with the reactor running at 20 MW. Three aliquots of this were analyzed by stepwise heating, using a defocused beam from a continuous Nd-YAG 1064 nm laser and the MAP 215-50 noble gas mass spectrometer at the University of Johannesburg's SPECTRUM analytical facility. This instrument is equipped with a Johnston focused-flow electron multiplier providing excellent linearity in analog mode. The amphibole standards McClure Mountains and Hb3GR as well as Fish Canyon Sanidine were used as monitors. Measurement control and data reduction was done using an in-house software suite that includes full error propagation by Monte Carlo procedures.

4. Clay mineral assemblage

Unlike illite, Fe-chlorite is not common in the lower, fluvial unit of FA (Figs. 2,3 and S1–S3). It is usually present near the base of the succession, (1) as a partial replacement of feldspar with illite and pyrite intergrowths (Fig. 3A and B); (2) dispersed in the inter-granular space (Fig. 3C) with illite, secondary monazite and huttonite (a Si-rich mineral of the monazite group) intergrowths (Fig. 3D), anhydrite and pyrite (Fig. 3E); (3) as fracture-fillings together with iron oxide and Sr-rich barite (Figs. 3F and 4A); (4) trapped in quartz cement and associated with pyrite (Fig. 4B).

Fe-chlorite is abundant in the fluvio-deltaic-tidal unit (Figs. 2,3 and S1–S4). Intergrown with illite, it commonly replaces detrital Fe-rich or ferromagnesian minerals, probably detrital spinels, such as hercynite (Figs. 4C and S5A,B) as indicated by the presence of exsolution lamellae and Ni-Cr-rich inclusions. Fe-chlorite also occurs: (1) in inter-granular spaces with illite (Figs. 4D and S5C), carbonate cement, rutile, iron oxide, secondary monazite and aluminum phosphate-sulfate (APS, an alteration product of monazite under oxic and acidic conditions (Gaboreau et al., 2005, 2007); Figs. 4C

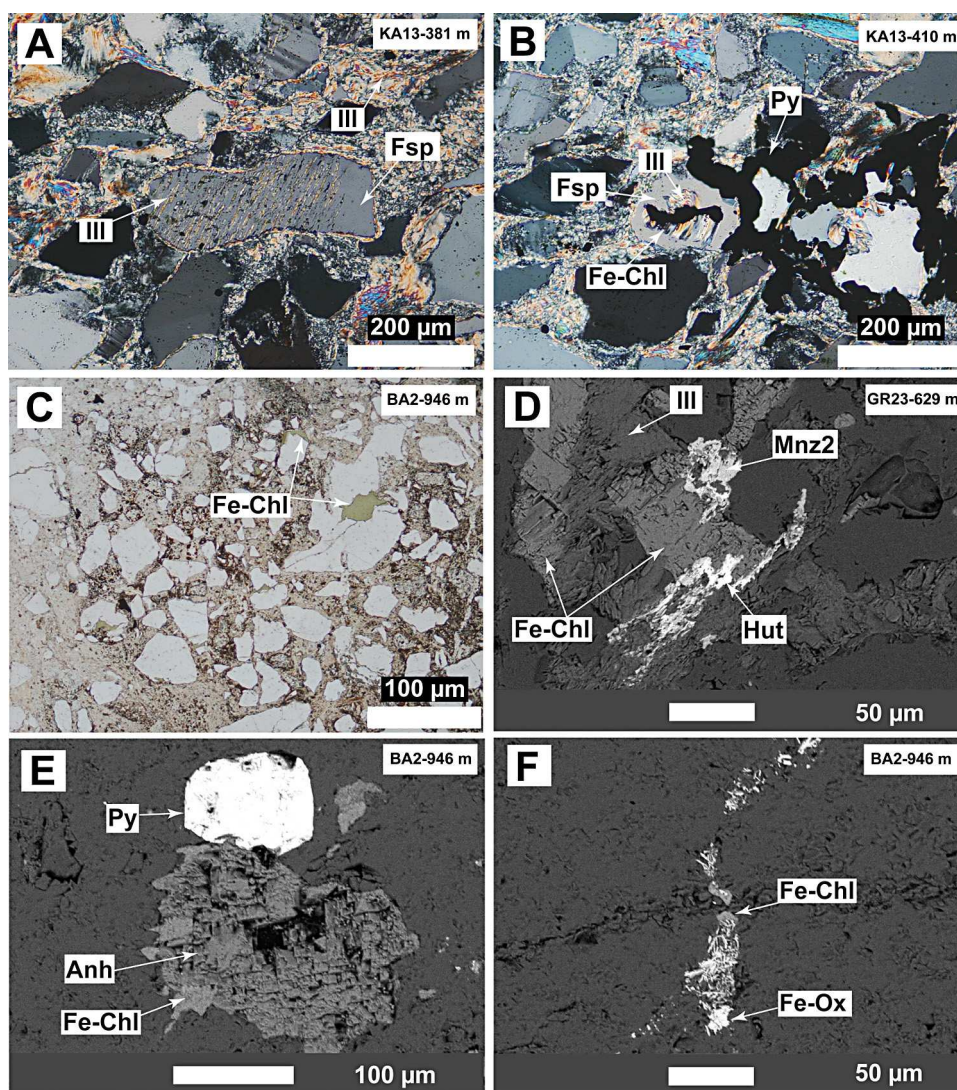


Fig. 3. Clay and associated mineral phases in the FA fluvial unit. (A) Photomicrograph showing formation of illite (Ill) as a partial replacement of clay matrix and partially dissolved feldspar (Fsp). (B) Photomicrograph showing Ill, Fe-chlorite (Fe-Chl) and pyrite (Py) intergrowths in intergranular space and as a partial replacement of Fsp. (C) Photomicrograph of Fe-Chl dispersed in clay matrix. (D) Backscattered electron image (BSE) of Ill and Fe-Chl associated with secondary monazite (Mnz2) and huttonite (Hut) intergrowths in intergranular space. E: BSE showing Py, anhydrite (Anh) and Fe-Chl intergrowths. F: BSE of Fe-Chl and iron oxide (Fe-Ox) as fracture filling.

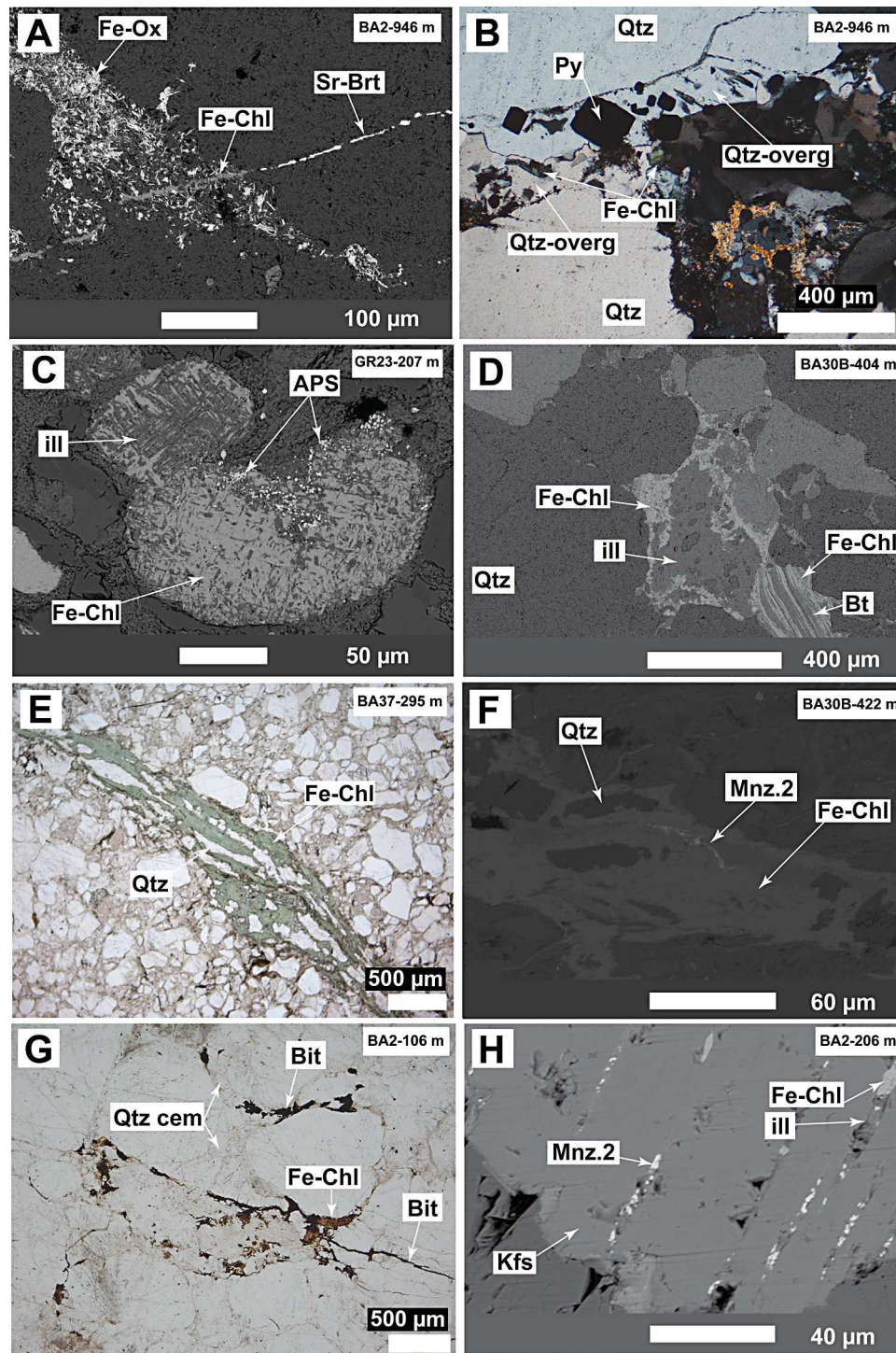


Fig. 4. Secondary mineral phases associated with neofomed clay minerals in the FA Formation. (A) BSE showing iron oxide (Fe-Ox) and cross-cutting fracture filled by Fe-chlorite (Fe-Chl) and Sr-rich barite (Sr-Brt). (B) Photomicrograph of idiomorphic pyrite (Py) and Fe-Chl in quartz overgrowths (Qtz-overg). (C) BSE showing total replacement of detrital ferromagnesian mineral now occupied by Fe-chlorite (Fe-Chl), illite (ill) and disseminated aluminum phosphate-sulfate (APS). (D) BSE of Fe-Chl with ill intergrowths in intergranular space, and detrital biotite (Bt) totally replaced by Fe-Chl and ill. (E and F) Fracture-filling Fe-Chl and quartz (Qtz) associated with secondary monazite (Mnz.2) in Fig. 3F. (G) Photomicrograph showing bitumen and Fe-chlorite as fracture filling, and in quartz cement. (H) Partially altered K-feldspar with secondary Fe-Chl, ill and elongate monazite (Mnz.2) aligned along the cleavage.

and S5D,E); (2) with quartz and secondary monazite in fracture-fillings (Fig. 4E and F), (3) with bitumen filling fractures or trapped within quartz cement (Figs. 4G, S5F,G), and with U-bearing galena and huttonite (Fig. S5H); (4) as a partial replacement of detrital K-feldspar together with illite and secondary monazite (Fig. 4H); (5) as a replacement of detrital mica (Fig. 4D).

Illite polytype is dominated by $1M_l$ -type (Fig. 5A), the formation of which requires a high fluid/rock ratio (Meunier and Velde, 2004). $2M_1$ -type of illite was also identified (Fig. 5A) and may indicate high fluid/rock ratios (e.g. Baronnet, 1982; Inoue and Kitagawa, 1994; Whitney, 1990), or detrital mica that is commonly found throughout the FA Formation. According to the $MR^{3+}-2R^{3+}-R^{2+}$ and

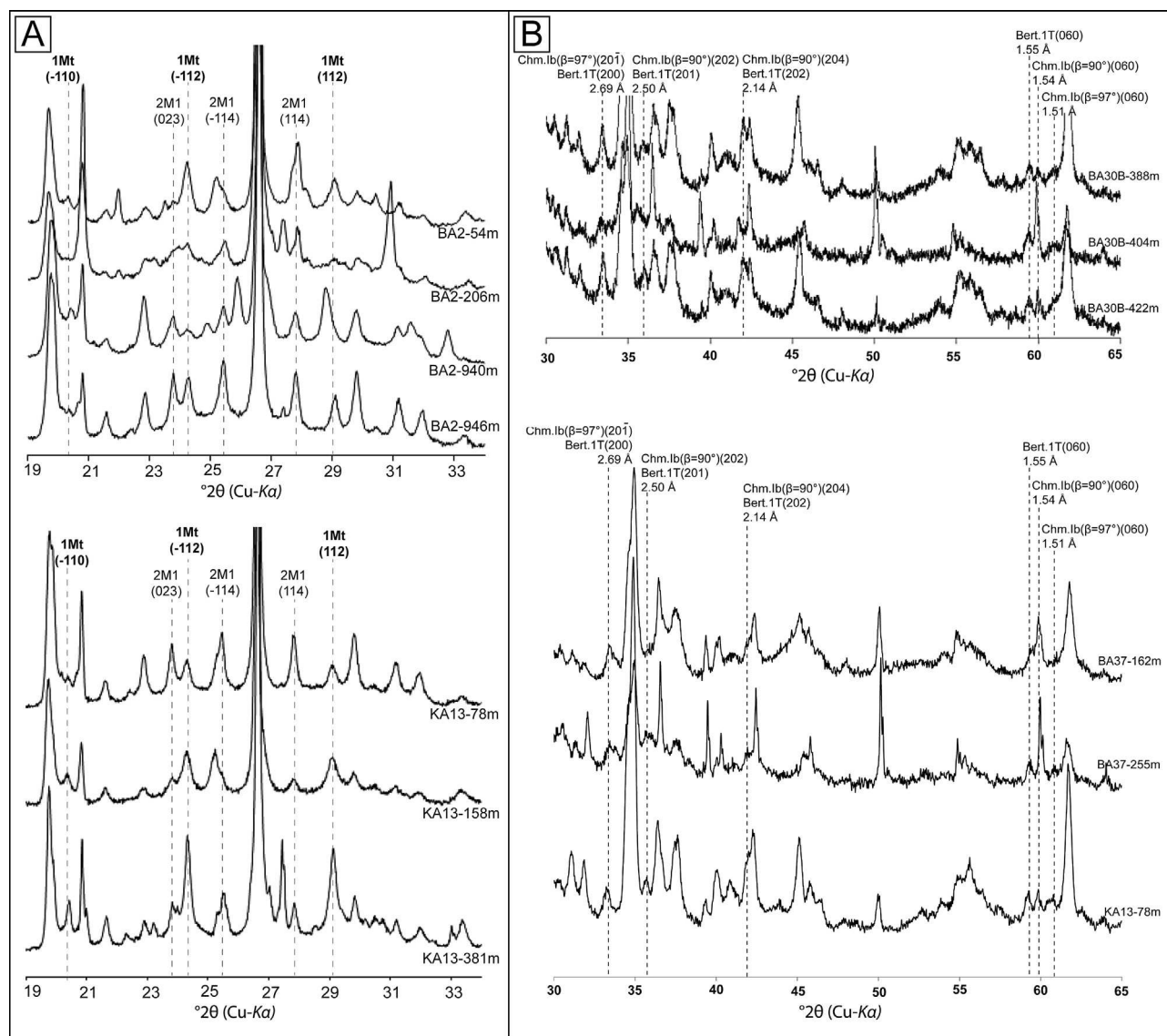


Fig. 5. XRD patterns of unoriented powders from FA clay fractions showing, (A) illite polytype species in BA2 (edge of basin) and KA13 (central part of basin) drill cores, and (B) main *hkl* reflections of Chm and Bert phases. Chm is characterized by Ib ($\beta = 97^\circ$ and $\beta = 90^\circ$) polytype species; Bert is characterized by 1T polytype species. Chm (chamosite), Bert (berthierine).

$M^{+}-4Si-R^{2+}$ triangular plots (Fig. 6A1 and A2), the chemical composition of illite (Table 1), calculated on the basis of 11 oxygens, corresponds to theoretical solid solution field of Al-rich illite, again characteristic for settings with a high fluid/rock ratio (Meunier, 2005; Meunier and Velde, 2004).

In order to distinguish 14 Å (e.g. Chm) and 7 Å (e.g. Bert) chlorite phases, heating tests were conducted on clay fractions concentrated by magnetic separation (Fig. 7). Indeed, unlike Chm (14 Å), Bert (7 Å) usually disappears after being heated at 550 °C (Brindley, 1961; Hornibrook and Longstaffe, 1996; Reynolds, 1985; Rivas-Sanchez et al., 2006). XRD patterns of heated, oriented powders of the magnetic fractions illustrate the disappearance of even-order chlorite peaks (7 and 3.53 Å), while the odd-order (14 and 4.74 Å) peaks flatten considerably or tend to disappear completely (Fig. 7B). According to Brindley (1961), Hornibrook and Longstaffe (1996), Reynolds (1985) and Rivas-Sanchez et al. (2006), such changes of diffraction peaks upon heating may suggest the presence of a 7 Å phase (e.g. Bert) and/or mixed layers characterized by a 14 Å phase (e.g. Chm) and 7 Å phases (e.g. Bert). Furthermore, according to the

characterization of diffraction peaks by Brindley and Brown (1980), XRD patterns of unoriented powders show $d_{060} = 1.54$ and 1.55 Å indicating respectively the presence of Ib (90° and 97°) Chm and 1T Bert polytypes (Fig. 5B). Because of the variation of XRD patterns, Newmod simulations (Reynolds, 1985) were made in order to estimate the mineral composition responsible for each type of XRD pattern morphology. Three main types of mineral composition were identified (Fig. S6): (1) type 1 characterized by Chm/Bert mixed layers with more than 50% of Bert content, including a pure Bert phase; (2) type 2 characterized by Chm/Bert mixed layers with Chm content ranging between 50% and 95%; (3) type 3 characterized by Chm/Bert mixed layers with more than 95% of Chm content, including a pure Chm phase. Their chemical composition (Table 2), calculated on the basis of 14 oxygens, has been plotted in the vector representation diagram of Wiewiora and Weiss (1990), which is used for the characterization of crystallo-chemical properties of chlorite (Fig. 6B1). The plot shows that most of the chlorites are trioctahedral, with a number of silicon atoms below 3 per formula unit and an octahedral charge ranging between 5.5

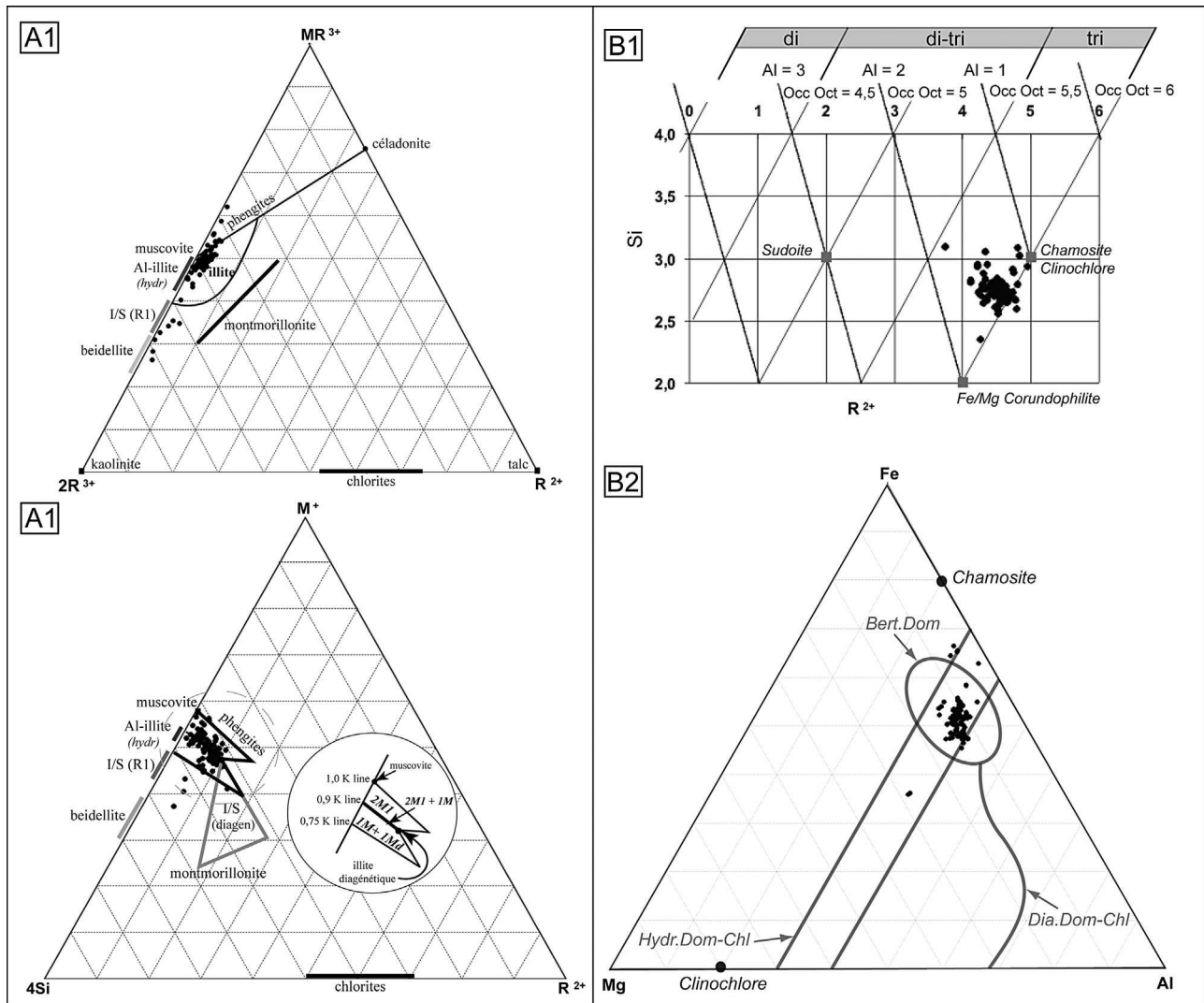


Fig. 6. Chemical composition of illite and Fe-chlorite phases (on the basis of 11 and 14 oxygens, respectively) from the FA Formation plotted on: (A1) $MR^{3+}-(Na^{+} + K^{+} + 2Ca^{2+})-2R^{3+}[(Al^{3+} + Fe^{3+})-(Na^{+} + K^{+} + 2Ca^{2+})]/2-R^{2+}(Mg^{2+} + Fe^{2+} + Mn^{2+})$ (Meunier and Velde, 2004); (A2) $M^{+}(Na^{+} + K^{+} + 2Ca^{2+})-4Si(\text{number ions } Si^{4+}/4)-2R^{+}[(Mg^{2+} + Fe^{2+} + Mn^{2+})/2]$ (Meunier and Velde, 2004); (B1) diagram of vector representation of Wiewiora and Weiss (1990); (B2) Magnesium-aluminum-iron (Mg-Al-Fe) diagram (compositional fields after Velde, 1985).

and 6 (Fig. 6B1). According to the Mg-Al-Fe triangular diagram plot (Fig. 6B2), the chemical composition of Fe-chlorite corresponds to theoretical solid solution fields of hydrothermal chlorites close to Bert and Chm domain (Velde, 1985).

As shown above, clay minerals including illite, Chm, Bert and Chm/Bert mixed layers are intergrown with alteration products of monazite, regarded as one of the primary U carrier phases (Cuney and Mathieu, 2000; Mathieu et al., 2001). According to EMP element maps, primary (detrital) monazite grains show secondary overgrowths (Figs. 8A and S7), which differ in REE and actinide concentrations (Figs. 8A and S7). For example, secondary monazites are characterized by higher concentrations of Ce, Nd and Y (Fig. 8A). Some overgrowths of monazite consist of contrasting types that differ in La and Ce concentrations (Fig. 8A1 and 8A6), suggesting that growth of secondary monazite took place under varying conditions. Primary and secondary monazites have low concentrations of U (Figs. 8A5, S7A3, S7B3 and S7C3), which either indicates leaching of U or primarily low U contents. However, U appears enriched in associated Chm, Bert, Chm/Bert mixed layers and illite phases (Figs. 8A5, S7A3, S7B3 and S7C3). This shows that U was a mobile phase that became fixed in clay mineral phases upon their growth.

5. Clay formation temperature estimates

In order to evaluate the thermal conditions in the FA Formation under which authigenic clay mineral formation and, by inference, dissolution-precipitation processes of U-bearing minerals took place, the formation temperatures of Chm were estimated using a thermodynamic approach. Several thermodynamic models allowing estimation of chlorite crystallization temperature have been published (Cathelineau, 1988; Cathelineau and Nieva, 1985; Inoue et al., 2009; Vidal et al., 2005, 2006; Walshe, 1986). In the case of Fe-chlorite, some of these models do not consider the Fe^{3+} content, which is likely to influence the temperature estimate by modifying the distribution of other elements such as Al in the crystalline structure of chlorite. The model of Vidal et al. (2005, 2006), based on multiple equilibria and which offers an adjustment of crystallization temperature by varying Fe^{3+} contents, can be used for metamorphic and/or hydrothermal chlorites which have less than 3 silicon atoms per formula unit calculated on the basis of 14 oxygens, including any natural assemblage and solid solutions involving chlorite.

In order to evaluate the effect of pressure on temperature estimates, the formation temperatures of Chm close to and far

Table 1

Chemical composition of illite phases close to and far away from reactor zones, determined by electron microprobe.

Samples ^a	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O
	(wt.%)								
Close to Bangombé reactor zone									
BA2-54m (n5)	37.93	23.96	24.00	4.28	0.01	1.42	0.16	0.27	7.95
BA2-54m (n4)	50.16	0.33	33.92	3.38	0.07	1.28	0.20	0.21	10.44
BA2-54m (n3)	49.23	0.45	33.02	4.52	0.05	1.37	0.12	0.21	11.04
BA2-54m (n2)	50.84	0.31	32.50	4.06	0.01	1.57	0.13	0.24	10.32
BA2-54m (n1)	51.01	0.25	31.38	4.42	0.00	1.87	0.10	0.20	10.77
BA30b-404m (n4)	44.76	0.26	25.90	4.07	0.04	1.67	0.14	0.16	8.89
BA30b-404m (n3)	40.33	0.40	24.61	3.75	0.02	1.32	0.06	0.15	9.10
BA30b-404m (n2)	44.32	0.20	24.68	4.71	0.00	1.70	0.15	0.17	8.74
BA30-404m (n1)	43.36	0.28	23.74	4.93	0.00	1.84	0.05	0.21	8.63
BA30b-422m (n3)	34.65	0.15	19.39	2.49	0.04	0.88	0.36	0.39	5.52
BA30b-422m (n2)	43.95	0.08	31.10	2.26	0.06	0.67	0.09	0.23	9.36
BA30b-422m (n1)	46.68	0.24	29.06	3.26	0.00	1.58	0.20	0.18	9.28
BA2-206m (n4)	51.20	0.18	32.74	3.84	0.03	1.71	0.14	0.31	9.85
BA2-206m (n3)	50.39	0.48	33.22	3.56	0.06	1.30	0.15	0.18	10.65
BA2-206m (n2)	49.61	1.49	33.28	3.12	0.00	1.28	0.11	0.27	10.85
BA2-206m (n1)	50.81	0.22	33.67	2.73	0.04	1.41	0.18	0.23	10.69
BA2-940m (n2)	49.78	0.05	37.37	0.34	0.11	0.93	0.26	0.30	10.86
BA2-940m (n1)	50.10	0.02	38.73	0.35	0.04	0.38	0.18	0.22	9.98
BA2-946m (n3)	48.28	0.07	38.44	0.01	2.14	0.27	0.07	0.30	10.38
BA2-946m (n2)	48.07	0.06	38.71	0.00	1.55	0.16	0.10	0.28	11.10
BA2-946m (n1)	49.10	0.00	37.43	0.00	2.91	0.20	0.23	0.33	9.82
Far away from reactor zones									
GR23-207m (n3)	41.43	0.30	30.06	4.66	0.06	1.14	0.08	0.21	8.50
GR23-207m (n2)	43.75	0.12	25.82	2.75	0.00	1.55	0.15	0.18	7.97
GR23-207m (n1)	45.37	0.12	29.08	2.21	0.01	1.06	0.22	0.26	8.47
GR23-629m (n1)	41.42	0.31	23.64	5.81	0.02	1.69	0.08	0.11	9.62
KA13-381 (n4)	43.36	1.14	27.15	2.66	0.00	1.51	0.18	0.18	9.20
KA13-381 (n3)	43.28	1.07	27.10	2.62	0.00	1.46	0.13	0.14	9.11
KA13-381 (n2)	41.66	0.27	28.96	1.44	0.00	0.88	0.14	0.17	9.10
KA13-381 (n1)	42.96	0.26	30.78	1.15	0.00	0.64	0.08	0.17	9.36
KA13-409 (n4)	43.81	0.03	31.93	0.82	0.00	0.49	0.13	0.23	9.27
KA13-409 (n3)	43.72	0.11	32.28	0.92	0.03	0.61	0.13	0.24	9.49
KA13-409 (n2)	41.37	0.15	29.79	0.87	0.00	0.67	0.11	0.23	9.23
KA13-409 (n1)	44.41	0.17	32.04	0.90	0.00	0.46	0.23	0.22	9.08

^a Samples: *n* = number of analysis of sample; BA30b = BA30bis.

away from reactor zones were estimated by varying the pressure, using values of 1 and 2 kbar. At 1 kbar, the calculated equilibrium temperatures range between 177 and 291 °C with an average of 235 ± 30 °C, and calculated Fe³⁺ contents (Fe³⁺/Fe_{total} (%)) range between 4 and 28% with an average of $17 \pm 7\%$ (Table 3). At 2 kbar, the equilibrium temperatures range between 186 and 299 °C with an average of 245 ± 30 °C, while Fe³⁺ contents have the same range (Table 3). The average temperature for the chosen pressures may be considered as ca. 240 ± 30 °C. No change was observed irrespective of the number of Chm analyses used, as well as correlation of estimate temperatures in both FA units near and far away from reactor zones. Furthermore, the temperature estimates and Fe³⁺ contents show negligible variations for the different pressure values used (Table 3). However, Fe³⁺ values of Chm show a net variation depending on the presence of bitumen. In bitumen-rich facies characterized by reducing conditions, the Fe³⁺ content of Chm is usually less than 10% of the total Fe content (e.g. sample OK110, Table 3). In facies lacking bitumen or containing APS and, thus, indicating more oxygenic conditions, Fe³⁺ content of Chm ranges between 13 and 28%, of total Fe (e.g. samples BA30bis, BA2, GR23, Table 3).

6. Timing of clay formation

The results of ⁴⁰Ar/³⁹Ar dating of illite from sample BA2-946 are listed in Table 4 and shown in Fig. 9. Traditionally, the use of this dating method on clays is viewed with skepticism, as grain sizes are not many orders of magnitude greater than the length of the recoil path of ³⁹Ar nuclei produced in irradiation (~80 nm, Villa,

1997), and this isotope might therefore be partially lost, resulting in an apparent age that is too high. However, in a dense aggregate and under vacuum, re-implantation of the recoiled nuclei into adjacent grains occurs (Huneke and Smith, 1976) and in the case of monomineralic aggregates, realistic plateau ages can be achieved (Dong et al., 1995, 1997). In our three dating experiments, the lowest temperature steps show ascending apparent ages between 1850 and 2000 Ma, which anticorrelate with Cl/K ratios indicating alteration (see figure caption for an explanation). Integrated plateau ages of 2033 ± 10 Ma, 2021 ± 10 Ma and 2023 ± 10 Ma were obtained. The overlap of error limits lends confidence to the result, which confirms that the formation of this clay phase is coeval with U mineralization.

7. Discussion

7.1. Spatial distribution of clay minerals at the regional scale

We suggest that the low iron availability, probably due to the lack of detrital Fe-rich and ferromagnesian minerals in the fluvial unit, hindered the formation of Chm and Bert, the occurrence of which is controlled by the availability of iron. Conversely, the abundance of former ferromagnesian minerals in the fluvio-deltaic-tidal unit would have favored the formation of Chm and Bert. These ferromagnesian minerals, spinels in particular, were probably erosional products of Archean mafic and ultramafic greenstone successions of the Chaillu or North-Gabon massifs (Fig. 1), and their presence indicates a possible change in the provenance of detrital input during deposition of the FA Formation, or some other change

Table 2

Chemical composition of Fe-rich clays close to and far away from reactor zones, determined by electron microprobe.

Samples ^a	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O
	(wt.%)								
Close to Oklo reactor zone									
OK110-360m (<i>n</i> 7)	22.81	0.01	20.86	40.86	0.06	1.84	0.00	0.03	0.06
OK110-360m (<i>n</i> 6)	22.97	0.02	21.76	38.95	0.12	2.56	0.04	0.05	0.15
OK110-360m (<i>n</i> 5)	22.46	0.06	20.55	39.80	0.05	1.95	0.02	0.04	0.05
OK110-360m (<i>n</i> 4)	23.81	0.04	21.29	36.58	0.11	2.24	0.02	0.05	0.37
OK110-360m (<i>n</i> 3)	23.63	0.04	21.68	37.25	0.11	3.66	0.05	0.06	0.09
OK110-360m (<i>n</i> 2)	23.03	0.03	20.61	35.79	0.09	3.73	0.02	0.04	0.03
OK110-360m (<i>n</i> 1)	23.00	0.00	21.27	35.10	0.12	3.77	0.05	0.04	0.13
Close to Bangombé reactor zone									
BA30b-404m (<i>n</i> 7)	23.40	0.05	18.36	33.76	0.00	5.09	0.05	0.15	0.37
BA30b-404m (<i>n</i> 6)	22.71	0.05	17.97	34.71	0.07	5.07	0.06	0.17	0.19
BA30b-404m (<i>n</i> 5)	24.14	0.06	19.02	35.11	0.10	5.84	0.03	0.17	0.04
BA30-404m (<i>n</i> 4)	22.50	0.00	19.06	33.47	0.09	4.67	0.05	0.16	0.45
BA30b-404m (<i>n</i> 3)	22.02	0.05	18.92	34.86	0.00	4.47	0.05	0.15	0.05
BA30b-404m (<i>n</i> 2)	21.16	0.00	17.22	34.24	0.00	4.20	0.06	0.13	0.09
BA30b-404m (<i>n</i> 1)	21.20	0.02	16.30	34.41	0.00	3.89	0.03	0.09	0.24
BA30b-422m (<i>n</i> 2)	20.52	0.10	16.90	34.49	0.10	3.74	0.03	0.11	0.05
BA30b-422m (<i>n</i> 1)	21.01	0.07	17.34	32.85	0.11	4.15	0.01	0.07	0.15
BA2-206m (<i>n</i> 2)	27.72	0.00	23.20	41.50	0.00	7.39	0.01	0.13	0.05
BA2-206m (<i>n</i> 1)	27.15	0.10	21.89	45.96	0.00	4.45	0.21	0.16	0.28
BA2-946m (<i>n</i> 1)	27.13	0.00	22.44	39.18	0.32	6.13	2.40	0.51	0.05
Far away from both reactor zones									
GR23-207m (<i>n</i> 6)	20.83	0.19	16.88	34.88	0.01	3.96	0.03	0.13	0.03
GR23-207m (<i>n</i> 5)	21.65	0.00	16.76	34.40	0.07	4.14	0.32	0.17	0.00
GR23-207m (<i>n</i> 4)	21.03	0.07	16.93	34.92	0.00	4.02	0.04	0.12	0.09
GR23-207m (<i>n</i> 3)	21.28	0.01	16.41	36.20	0.00	3.58	0.10	0.17	0.04
GR23-207m (<i>n</i> 2)	22.52	0.07	18.83	34.37	0.03	4.34	0.01	0.08	0.26
GR23-207m (<i>n</i> 1)	21.15	1.65	16.21	34.64	0.00	4.22	0.03	0.11	0.02
GR23-629m (<i>n</i> 1)	22.10	0.00	17.5	24.80	0.40	10.90	0.30	0.20	0.02

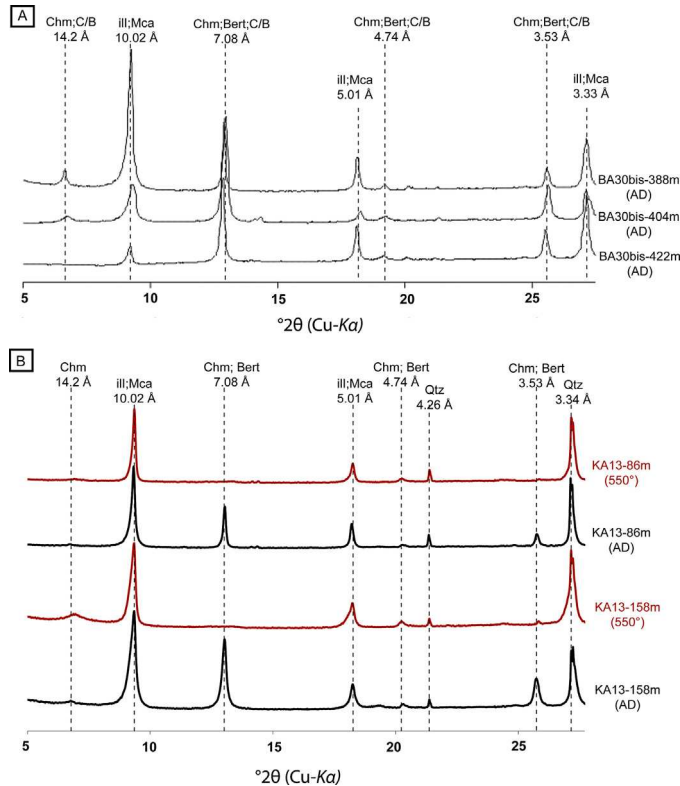
^a Samples: n = number of analysis of sample; BA30b = BA30bis.

Fig. 7. XRD patterns of oriented powders of FA clay fractions concentrated by magnetic separation (Fe-rich clays). (A) Air-dried (AD) Fe-rich clays sampled near to natural nuclear reactor zone (edge of basin). (B) Samples of AD and heated (550°C) Fe-rich clays far from natural nuclear reactor zone (central part of basin). Chm (chamosite), Bert (berthierine), ill (illite), Mca (mica), Qtz (quartz).

that had an influence on the sandstone composition, such as climate or level of reworking. Even if the relationship between Chm and Bert remains uncertain, the presence of their distinct polytype species shows that these mineral phases would have co-existed together with illite in the fluvio-deltaic-tidal unit. Syn-depositional tectonism associated with Francevillian basin evolution was complex, making lithostratigraphic correlations at the regional scale difficult (Azzibrouck-Azziley, 1986; Pambo et al., 2006; Pr  at et al., 2011; Thi  blemont et al., 2009). The latter are fundamental for the mining industry in the Francevillian basin, which has been a major producer of U from the FA Formation. We suggest that the spatial distribution of clay minerals may be helpful for better constraining lithostratigraphic correlation. A clay assemblage characterized by the predominance of illite might be a potential mineralogical marker for the regional distribution of the fluvial unit, and the more diversified clay assemblage of illite, Chm, Bert and C/B could characterize the fluvio-deltaic-tidal unit hosting U ore deposits (Fig. 10).

In areas where alteration products of U-bearing minerals are represented by Mnz.2, Hut, APS, F-ap and sulfate (anhydrite and Sr-rich barite), both detrital and secondary monazites are relatively U-poor (e.g. Figs. 8 and S7), and Chm is characterized by Fe³⁺ contents as high as 28% relative to its total Fe content (Table 3). This illustrates possible leaching and migration of U during the dissolution-crystallization process under relatively oxic conditions, the signature of which is marked by the formation of APS, as previously shown by Gaboreau et al. (2005, 2007) from uranium deposits of the Northern Territory in Australia and the Athabasca basin in Canada. In areas characterized by the presence of bitumen, the occurrence of relatively U-rich minerals (e.g. U-rich galena) is common, and the Fe³⁺ contents within associated Chm is mostly lower than 10% relative to its total Fe content (Table 3). The latter shows a possible precipitation of U-rich minerals under more reducing conditions (Gauthier-Lafaye and Weber, 1989; Mathieu et al., 2000). In view of this, Fe³⁺ content associated with chlorite phases could

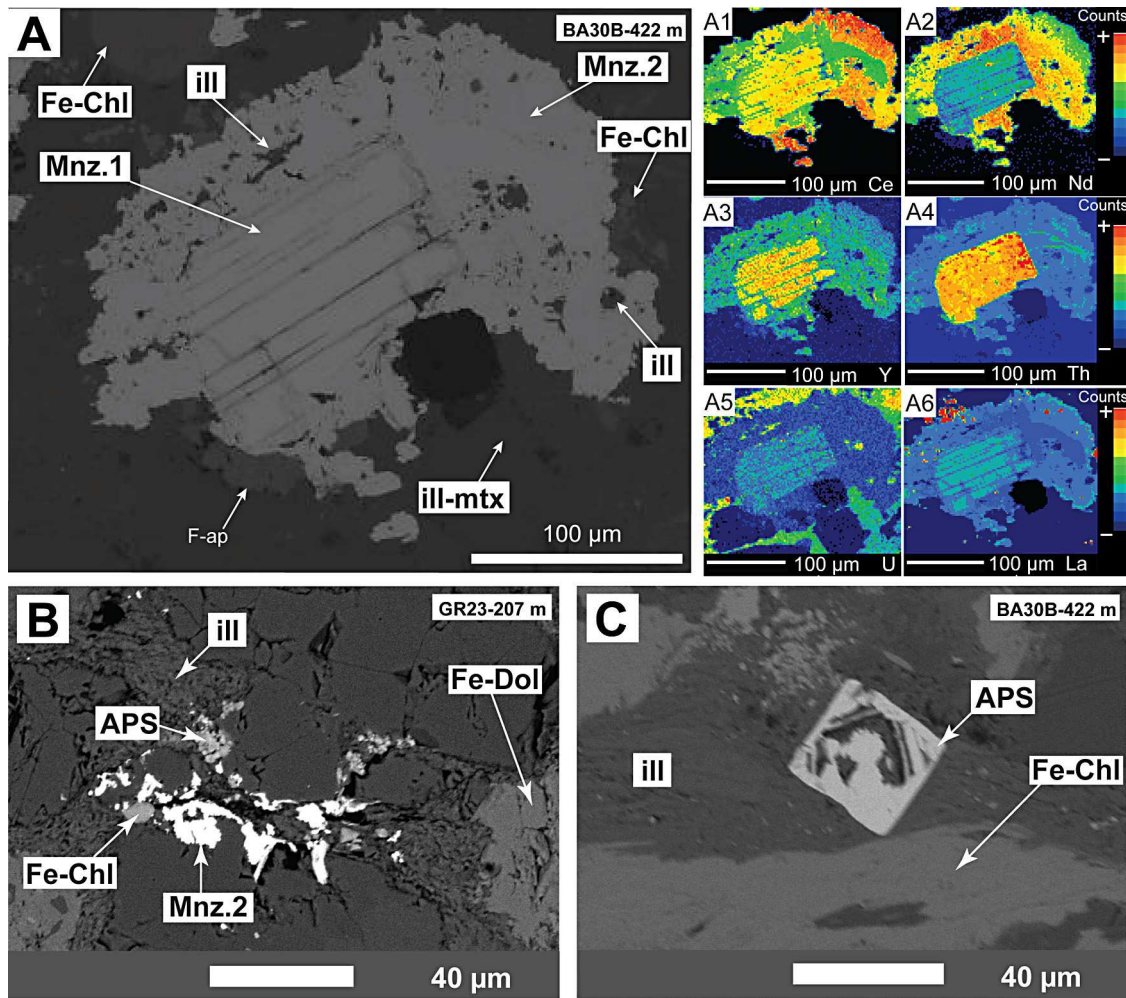


Fig. 8. Alteration processes of U-bearing minerals. (A) BSE of detrital monazite (Mnz.1) showing overgrowth of secondary monazite (Mnz.2) together with neoformed illite (ill) and fluorapatite (F-ap); (A1–A6) X-ray maps of selected elements where U appears to be concentrated in neoformed clay minerals (A5). (B) BSE of intergranular space filled by Fe-chlorite (Fe-Chl), Fe-rich dolomite cement (Fe-Dol), illite (ill), as well as secondary monazite (Mnz.2) and aluminum phosphate-sulfate (APS). (C) BSE showing APS, ill and Fe-Chl intergrowths in intergranular space.

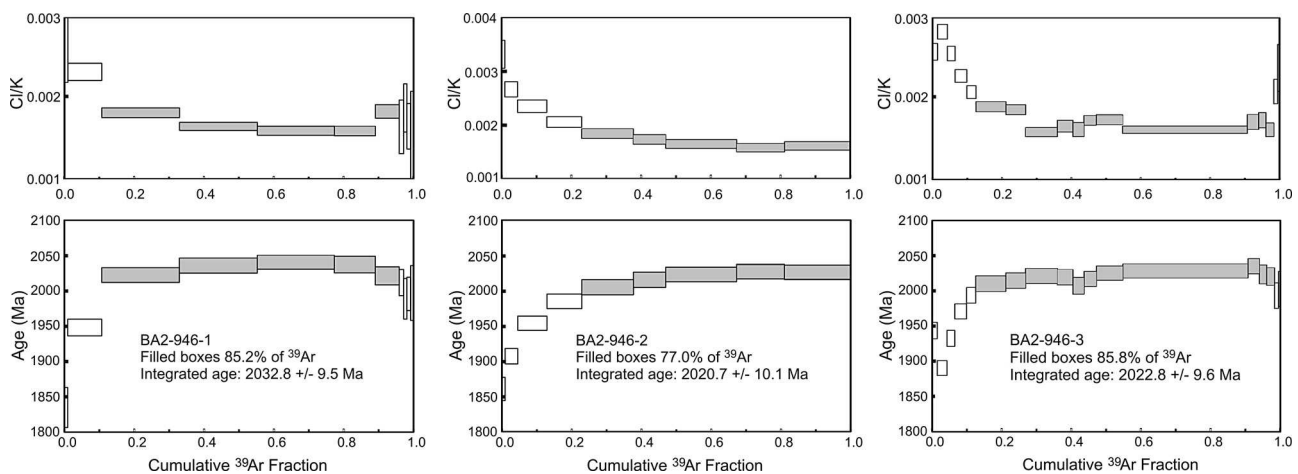


Fig. 9. Age and associated Cl/K spectra (obtained from $^{38}\text{Ar}/^{39}\text{Ar}$ ratios, reaction $^{37}\text{Cl}(n,e)^{38}\text{Ar}$), of three aliquots of the <2 μm illite fraction from sample BA2-946, obtained using different step heating protocols (temperature difference between heating steps decreases from ~100 °C for BA2-946-1 to ~50 °C for BA2-946-3; see Table 4). Error boxes reflect 95% confidence limits. Note low apparent ages at low temperature steps and consistent anticorrelation of Cl/K ratios with apparent ages: higher Cl contents reflect altered regions or different phases, from which ^{40}Ar is more easily lost (Dong et al., 1997), or more likely, an alteration event that occurred at, or up to about 1850 Ma. The general anticorrelation of Cl/K against apparent age indicates that small variations in the plateaus are not caused by ^{39}Ar recoil loss. This is so because the recoil distance of ^{38}Ar from Cl is ca 1000× smaller than that of ^{39}Ar from K (Onstott et al., 1995; Villa, 1997). Therefore recoil loss, diminishing ^{39}Ar but not ^{40}Ar or ^{38}Ar , would produce a positive correlation of apparent ages and Cl/K ratios instead of the anticorrelation observed. We conclude that ^{39}Ar recoiled out of grains was wholly re-implanted in neighboring grains, and the plateau ages obtained are valid.

Equilibrium temperatures and Fe³⁺ contents of chamosite and berthierine (after thermodynamic model of Vidal et al., 2005, 2006).

Samples*	†Pressure (1 kbar)		†Pressure (2 kbar)	
	Temperature (°C)	Fe ³⁺ /Fe _{total} (%)	Temperature (°C)	Fe ³⁺ / Fe _{total} (%)
Close to Oklo reactor zone				
OK110-360m (n7)	291	4	299	4
OK110-360m (n6)	277	4	287	4
OK110-360m (n5)	279	5	291	5
OK110-360m (n4)	178	17	189	16
OK110-360m (n3)	250	8	260	8
OK110-360m (n2)	238	10	252	9
OK110-360m (n1)	244	8	250	8
Close to Bangombé reactor zone				
BA30bis-404m (n7)	239	13	253	16
BA30bis-404m (n6)	232	19	241	19
BA30bis-404m (n5)	217	25	227	25
BA30bis-404m (n4)	177	28	186	28
BA30bis-404m (n3)	217	25	227	25
BA30bis-404m (n2)	199	22	224	25
BA30bis-404m (n1)	203	25	214	25
BA30bis-422m (n2)	255	13	267	16
BA30bis-422m (n1)	217	16	236	19
BA2-206m (n2)	252	16	260	16
BA2-206m (n1)	224	19	233	19
BA2-946m (n1)	225	25	236	25
Far away from both reactor zones				
GR23-207m (n6)	250	16	260	16
GR23-207m (n5)	213	22	224	22
GR23-207m (n4)	242	19	250	19
GR23-207m (n3)	230	22	239	22
GR23-207m (n2)	202	19	211	19
GR23-207m (n1)	283	19	291	19
GR23-629m (n1)	278	25	288	25

[†] Pressure: Fixed pressure to estimate the equilibrium temperature in the thermodynamic model of [Vidal et al. \(2005, 2006\)](#).

Temperature (°C) = equilibrium temperatures calculated for a pressure of 1 kbar (§) and 2 kbar (§§); Fe³⁺/Fe_{total} (%) = ratio of Fe³⁺ compared to the total iron in chamosite and berthierine, estimated for a pressure of 1 kbar (§) and 2 kbar (§§).

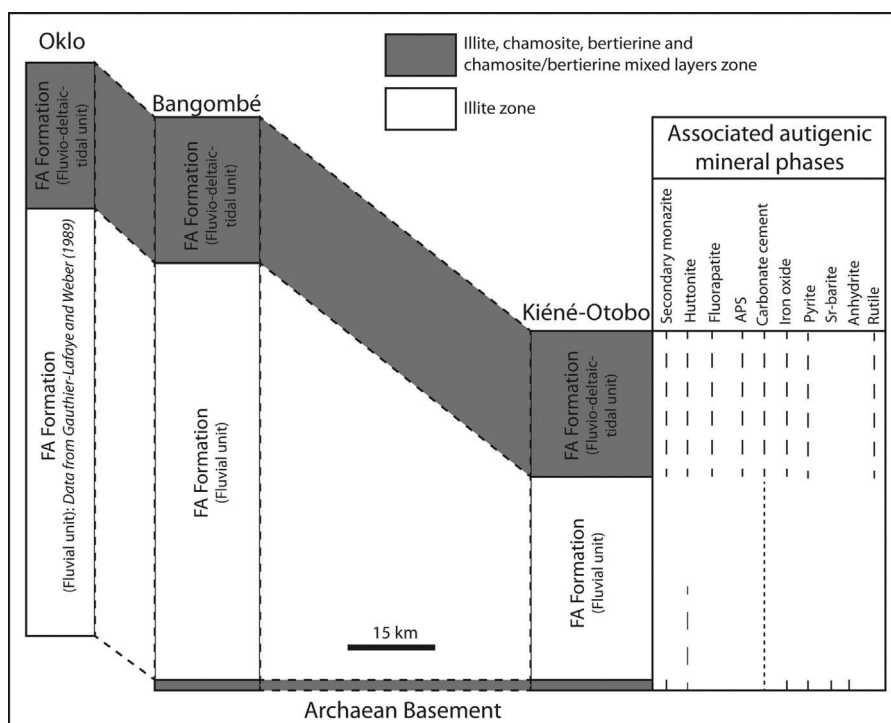


Fig. 10. Spatial distribution of clay formation and associated mineral phases in the FA Formation at the scale of Franceville sub-basin.

Table 4
Results of argon step heating analyses.

$T(^{\circ}\text{C})^{\text{a}}$	cc stp ^{39}Ar	% ^{39}Ar	Included ^b	Age Ma $\pm$ 95%	Ca/K	Cl/K $\pm$ 95%
BA2-946-1						
500	4.09E–12	0.95	No	1834.8 $\pm$ 28.4	<0.01	0.0032 $\pm$ 0.0010
610	4.19E–11	9.72	No	1948.2 $\pm$ 11.9	<0.01	0.0023 $\pm$ 0.0001
720	9.60E–11	22.26	Yes	2022.5 $\pm$ 10.4	<0.01	0.0018 $\pm$ 0.0001
830	9.62E–11	22.31	Yes	2036.1 $\pm$ 10.7	<0.01	0.0016 $\pm$ 0.0001
950	9.52E–11	22.08	Yes	2040.7 $\pm$ 9.7	<0.01	0.0016 $\pm$ 0.0001
1070	5.06E–11	11.73	Yes	2037.5 $\pm$ 11.8	<0.01	0.0016 $\pm$ 0.0001
1190	2.94E–11	6.81	Yes	2021.5 $\pm$ 12.7	<0.01	0.0018 $\pm$ 0.0001
1300	5.58E–12	1.29	No	2011.9 $\pm$ 18.5	<0.01	0.0016 $\pm$ 0.0003
1380	4.00E–12	0.93	No	1989.0 $\pm$ 28.7	<0.01	0.0019 $\pm$ 0.0003
1430	4.60E–12	1.07	No	1995.9 $\pm$ 23.6	<0.01	0.0017 $\pm$ 0.0003
1480	3.67E–12	0.85	No	1997.2 $\pm$ 38.9	<0.01	0.0014 $\pm$ 0.0007
BA2-946-2						
500	1.11E–11	0.92	No	1861.0 $\pm$ 16.5	<0.01	0.0033 $\pm$ 0.0003
590	4.41E–11	3.63	No	1907.6 $\pm$ 10.9	<0.01	0.0027 $\pm$ 0.0001
680	1.02E–10	8.39	No	1954.3 $\pm$ 10.2	<0.01	0.0024 $\pm$ 0.0001
770	1.21E–10	9.95	No	1985.5 $\pm$ 10.4	<0.01	0.0021 $\pm$ 0.0001
860	1.80E–10	14.81	Yes	2005.5 $\pm$ 10.8	<0.01	0.0018 $\pm$ 0.0001
950	1.12E–10	9.26	Yes	2016.1 $\pm$ 10.9	<0.01	0.0017 $\pm$ 0.0001
1040	2.47E–10	20.31	Yes	2023.5 $\pm$ 10.3	<0.01	0.0016 $\pm$ 0.0001
1130	1.67E–10	13.72	Yes	2027.7 $\pm$ 10.3	<0.01	0.0016 $\pm$ 0.0001
1220	2.30E–10	18.93	Yes	2026.6 $\pm$ 10.2	<0.01	0.0016 $\pm$ 0.0001
1320	1.02E–12	0.08	No	1923.8 $\pm$ 66.0	<0.01	0.0033 $\pm$ 0.0020
BA2-946-3						
500	1.50E–11	1.43	No	1943.8 $\pm$ 11.7	<0.01	0.0026 $\pm$ 0.0001
550	2.95E–11	2.81	No	1890.5 $\pm$ 10.5	<0.01	0.0028 $\pm$ 0.0001
600	2.34E–11	2.23	No	1932.6 $\pm$ 11.4	<0.01	0.0026 $\pm$ 0.0001
650	3.57E–11	3.40	No	1971.0 $\pm$ 10.6	<0.01	0.0023 $\pm$ 0.0001
700	2.75E–11	2.62	No	1993.7 $\pm$ 11.1	<0.01	0.0021 $\pm$ 0.0001
750	9.08E–11	8.65	Yes	2010.3 $\pm$ 11.1	<0.01	0.0019 $\pm$ 0.0001
800	5.96E–11	5.68	Yes	2014.6 $\pm$ 10.9	<0.01	0.0019 $\pm$ 0.0001
850	9.59E–11	9.14	Yes	2021.1 $\pm$ 10.7	<0.01	0.0016 $\pm$ 0.0001
900	4.69E–11	4.47	Yes	2019.3 $\pm$ 10.8	<0.01	0.0017 $\pm$ 0.0001
950	3.34E–11	3.19	Yes	2007.2 $\pm$ 11.9	<0.01	0.0016 $\pm$ 0.0001
1000	3.72E–11	3.55	Yes	2017.0 $\pm$ 10.6	<0.01	0.0017 $\pm$ 0.0001
1050	7.96E–11	7.58	Yes	2025.2 $\pm$ 10.1	<0.01	0.0017 $\pm$ 0.0001
1100	3.77E–10	35.95	Yes	2028.3 $\pm$ 9.9	<0.01	0.0016 $\pm$ 0.0001
1150	3.43E–11	3.27	Yes	2035.0 $\pm$ 10.7	<0.01	0.0017 $\pm$ 0.0001
1200	2.20E–11	2.10	Yes	2023.4 $\pm$ 13.3	<0.01	0.0017 $\pm$ 0.0001
1250	2.36E–11	2.25	Yes	2020.3 $\pm$ 12.4	<0.01	0.0016 $\pm$ 0.0001
1300	1.20E–11	1.14	No	1993.3 $\pm$ 18.1	<0.01	0.0021 $\pm$ 0.0002
1350	5.60E–12	0.53	No	2002.8 $\pm$ 24.9	<0.01	0.0024 $\pm$ 0.0003

^a Temperatures are optically estimated and approximate.

^b Included in calculation of integrated plateau age. Abundances and isotope ratios were extrapolated to the time of gas entry into the mass spectrometer and blank corrected. Typical blank values at entry time were 3×10^{-14} and 10^{-11} cc stp for ^{39}Ar and ^{40}Ar , respectively.

represent a chemical-mineralogical marker of the spatial evolution of redox conditions, which ultimately controlled the mobilization and precipitation of U in the FA Formation.

Characterization of radiation-induced defects in clay mineral phases in the FA Formation, including illite and Chm, by electron paramagnetic resonance spectroscopy showed that clay formation was prior to, or synchronous with, the migration of radioelements (Ossa Ossa, 2010). New observations of the redistribution of U in clay mineral phases (Figs. 5A5, 5A3, 5B3 and 5C3) sheds new light on this proposition. Radiation-induced defects in clay minerals and their dosimetry are potentially relevant for the quantitative reconstruction of past migrations of radioelements in geological systems (Morichon et al., 2008, 2010). Their formation in clay minerals could be potentially relevant for the quantitative reconstruction of losses and accumulations of radioelements in the FA Formation. This new possibility, together with Fe^{3+} content in chlorite, may be helpful in future exploration for U mineralization in the Francevillian basin.

7.2. Paleo-thermicity associated with clay formations

We estimated that Chm formed at an average temperature of ca. $240 \pm 30^{\circ}\text{C}$. No trend in estimated temperature was observed both

vertically in the succession and laterally, in terms of proximity to natural nuclear reactors, although the thermal perturbation around the center of the reactors was estimated not to have extended for more than 50 m in these natural laboratories operating over ca. 2 Ga (Royer et al., 1995 as referenced by Gauthier-Lafaye et al., 1996). These estimates are in agreement with temperature estimates (ca. 180 and 240°C) obtained by microthermometry on fluid inclusions in quartz cement and interpreted as a result of late diagenesis (Gauthier-Lafaye and Weber, 1989; Mathieu et al., 2000). These temperatures indicate a geothermal gradient between ca. 40 and $60^{\circ}\text{C}/\text{km}$ using the maximum burial estimate of 4100 m for the top of FA (Gauthier-Lafaye and Weber, 1989). A fundamental issue is to evaluate if the normal evolution of burial diagenesis itself could have allowed to reach such relatively high temperature in the Franceville sub-basin as previously described (Gauthier-Lafaye and Weber, 1989; Mathieu et al., 2000).

During deposition of the FA and FB formations, the Franceville sub-basin was an intracratonic basin subjected to extension, with mechanical subsidence controlled by NW-SE and N-S trending faults (Gauthier-Lafaye and Weber, 1989, 2003). A typical geothermal gradient of extensive intracratonic post-Archean sedimentary basins is $30^{\circ}\text{C}/\text{km}$ (e.g. Meunier, 2005; Velde, 1995) as shown in the case of the Athabasca basin, Thelon basin, Mc Arthur basin

(Hiatt et al., 2007), or the Paris basin (Velde and Vasseur, 1992). Therefore a geothermal gradient between ca. 40 and 60 °C/km estimated for the Franceville sub-basin appears unusually high. An explanation for the apparently high geothermal gradient may be an underestimation of the maximum burial of the top of the FA Formation (4100 m) as obtained by extrapolation and using various published geothermobarometers (Gauthier-Lafaye and Weber, 1989; Openshaw et al., 1978). However, in a sedimentary succession that experienced a burial greater than 5000 m (the inferred burial depth of the base of the FA Formation), Chm 11b or 1a polytype species (Ryan and Hillier, 2002; Ryan and Reynolds, 1996) and the 2M₁ structure as the dominant polytype species of in situ illite phases (Meunier and Velde, 2004), would be expected. Yet, such markers are not present even in the lowermost part of the FA Formation, suggesting that the maximum burial depth of the FA Formation may even have been overestimated.

Several studies have shown that a high geothermal gradient found in some extensional sedimentary basins may be due to a thermal anomaly related to hydrothermal fluid flow close to volcanic heat sources, as for example shown by Mathieu and Velde (1989) and Velde and Lanson (1993) in the case of the Paris Basin. Another possibility could be an elevated crustal heat flow during the Palaeoproterozoic in general, and in the Francevillian Basin in particular. Extension of the crust to provide accommodation space for the FA/FB formations may have taken place together with thinning of the mantle lithosphere giving rise to a higher heat flux from the mantle, while magmatic underplating of the crust may have heralded the onset of FD/FE magmatism further increasing crustal heat flow. As the availability of geophysical data for the basement beneath the Francevillian basin is limited, the elevated geothermal gradient may best be related to syndepositional volcanic activity. Evidence for volcanic activity is widespread in the Francevillian basin, as indicated by volcanic and volcanoclastic rocks associated with the FD and FE formations (Weber, 1968), recently dated at 2083 ± 6 and 2072 ± 29 Ma for FD and at 2021 ± 18 Ma for FE (Préat et al., 2011; Thiéblemont et al., 2009). Volcanic rocks of the complex of N'goutou have been dated, albeit imprecisely, at 2143 ± 143 Ma (Bonhomme et al., 1982) and 2027 ± 55 Ma (Moussavou and Edou-Minko, 2006). Although direct evidence is absent, the overlap in timing between hydrothermal clay formation, monazite and zircon alteration, U mineralization and volcanic activity in the Francevillian basin between ca. 2040 and 2010 Ma opens a new perspective that links volcanism to a high geothermal gradient, hydrothermal activity and, ultimately, U mineralization.

Despite the inferred high geothermal gradient, the preservation of expandable sedimentary and early diagenetic clay minerals (Bros et al., 1992; Ossa Ossa et al., 2013; Stille et al., 1993), including R0- and R1-type illite/smectite mixed layers, in the overlying FB Formation (Ossa Ossa et al., 2013), suggest that the Francevillian successions remained in the realm of diagenesis, not metamorphism, and that it experienced sluggish burial diagenesis. Mineral transformation processes were mainly controlled by fluid-rock interactions and were more pronounced in facies with high porosity and permeability such as sandstone and conglomerate (Ossa Ossa et al., 2013). Diagenesis played an important role in the thermal history of the Franceville sub-basin. However, in the FA Formation and at the scale of the Franceville sub-basin, hydrothermal activity probably overprinted and masked other events. In addition to diagenetic processes, hydrothermal activity would have given rise to mineral transformation under high fluid/rock ratio as well as intensified fluid flow, remobilizing U at quantities higher than estimated for burial diagenesis alone (e.g. Cuney and Mathieu, 2000; Mathieu et al., 2001). The combined petrographic, mineralogical, thermodynamic and geochronological data suggest that occurrence of clay minerals in the FA Formation could be considered as a hygrometer, rather than exclusively a thermometer. The signature of the

mobilization of large amounts of U, marked by the formation of U-rich clays, would have been the result of a combination of high fluid/rock ratios and high temperature, likely controlled by oxidizing conditions and volcanic activity, respectively. In the case that the inferred hydrothermal activity involved an external heat source, one could also consider potential external U sources, including volcanic rocks and rocks of the Archean basement. New perspectives for the origin of U deposits in the Francevillian basin, also characterized by natural nuclear reactors, can thus be considered.

8. Conclusion

Clay mineralogy suggests widespread hydrothermal activity in the FA Formation of the Franceville sub-basin of Gabon. This hydrothermal activity was associated with clay mineral formation with a distinct spatial distribution. Clay minerals in the lower fluvial unit of the FA Formation are mainly represented by illite, while the overlying fluvio-deltaic-tidal unit is characterized by the occurrence of illite, Chm, Bert and C/B. The distinct spatial distribution can be used as a mineralogical marker for a better understanding of the lithostratigraphic subdivision and the distribution of FA-hosted U mineralization in this sedimentary basin.

The crystallization of illite, Chm, Bert and C/B is synchronous with quartz cementation, oil migration and dissolution-precipitation processes of U-bearing accessory minerals. Clay minerals are enriched in U, suggesting that clay mineral formation, migration of U-rich fluids, and precipitation of U-rich minerals has taken place under the same conditions. Thermodynamic modeling using the chemical composition of Chm and geochronology performed on associated illite show that clay formation and associated alteration processes occurred at average temperatures of ca. 240 ± 30 °C, between ca. 2040 and 2010 Ma. Taken together with estimates of maximum burial of ca. 4100 m suggest hydrothermal activity possibly involving an external heat sources associated with volcanism during deposition of the upper part of the Francevillian Group. In the absence of metamorphic effects, the predominance of 1M₁ polytype of illite illustrates alteration processes in an environment controlled by a high fluid/rock ratio, while its association with APS intergrowths and Fe³⁺ content of Chm indicates changes in redox conditions, controlling migration and precipitation of U during burial and hydrothermal activity. The thermal history of the FA Formation proposed here opens a new window for a better understanding of the origin and conditions in which U deposits occurred, and may warrant re-evaluation of U reserves in the Francevillian basin. However, work remains to be done in the characterization of the exact nature of the hydrothermal processes. Further surface and subsurface studies of the basement rocks are warranted, in order to better constrain the type of hydrothermalism involved, the possible heat source, and the ultimate source of U.

Acknowledgments

This study was funded by the French Embassy at Libreville, the French Ministry for foreign affairs, the University of Johannesburg, the National Research Foundation of South Africa (Research fellowship and Grant 75892 to A. Hofmann), the University of Poitiers and the French CNRS-INSU. We thank the Ministry of Mines and Industry, COMILOG SA and SYSMIN Project (BRGM) from Gabon for assistance and collaboration. For discussion, we thank, François Gauthier-Lafaye, Francis Weber, Denis Thiéblemont, Florent Pambo, Daniel Beaufort, Martine Buatier, Alain Trentesaux, Sabine Petit, Maurice Pagel, Paul Sardini, Bruno Lanson, Boris Sakharov, Jean-Pierre Milesi, Eric Ferrage, Dominique Proust, Michel Cuney, Michel Cathelineau, Jean Louis Feybesse and Olivier Parize.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.precamres.2014.03.003>.

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