

Natural nuclear fission reactors: time constraints for occurrence, and their relation to uranium and manganese deposits and to the evolution of the atmosphere

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Abstract

Knowledge of the formation conditions of Francevillian uranium and manganese ore deposits as well as natural fission reactors sheds light on the early evolution of the atmosphere between 1950 and 2150 Ma ago. The model explaining the formation of the Oklo uranium deposits suggests that at the time of sediment deposition in the Franceville basin 2150 million years ago, the oxygen deficient atmosphere would have inhibited uranium dissolution. Dissolution of uranium was only possible during later diagenesis, approximately 1950 Ma. Reduction reactions in the presence of hydrocarbons allowed precipitation of dissolved uranium to U^{4+} , forming deposits with high enough uranium contents to trigger subsequent nuclear fission reactions. Such a model is in agreement with earlier suggestions that oxygen contents in atmosphere increased during a 'transition phase' some 2450–2100 Ma ago. The manganese deposits were formed before the uranium deposits, during the deposition of the black shales and very early diagenesis, and thus at a time when oxygen content in atmosphere was very low. Carbon isotopes data of organic matter show decrease of $\delta^{13}C$ upward in the Francevillian series (–20 to –46‰ PDB) reflecting the high CH_4 and low O_2 contents in the atmosphere during sediment deposition. This favoured anoxic conditions during deposition of the basinal FB black shales and likewise the migration of Mn over long distances. The manganese precipitated first as Mn-oxides at the shallow edges of the Franceville basin, in photic zones, where photosynthetic organisms flourished. Mn-oxides were then reduced in the black shales forming Mn-carbonates when conditions became more reducing during transgression episodes and/or the first stages of burial. In the black shales, reducing conditions prevailed until recent weathering, allowing the good preservation of organic matter and the Mn deposits. The present-day alteration is responsible for the dissolution of Mn-carbonates and precipitation of Mn-oxides at the water table to form the high grade Mn ore (45–50% Mn). Development of photosynthesizing organisms, a volcanic source of the Mn, and favourable palaeogeography of the Francevillian basins are all important parameters for the formation of the Mn deposits. For the occurrence of the natural nuclear reactors, the age of 2.0 Ga is the main parameter that controls the abundance of fissile ^{235}U and the critical mass. Before 2.0 Ga the $^{235}U/^{238}U$ ratio was sufficiently high for fission reactions to occur but conditions favourable for forming high grade uranium ores were not achieved. Then, after 2.0 Ga the increase of oxygen in the atmosphere commonly led to the formation of high grade uranium ores in which the $^{235}U/^{238}U$ ratio was too low to support criticality.

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1. Introduction

The natural nuclear fission reactors in Gabon are unique. The possibility that nuclear fission reactions might have occurred in the past was first suggested by Kuroda 1956 but we had to wait until 1972 to discover that such reactions did indeed occur 2.0 Ga ago in the Oklo uranium deposit of the Francevillian Series, Gabon (Neuilly et al., 1972). Other uranium deposits of Proterozoic age in the world (Maas and McCulloch, 1990) do not manifest the characteristic U and REE isotopic anomalies of natural nuclear fission reactions, suggesting that these only occurred in the Paleoproterozoic uranium ore deposits of Gabon. This observation raises the question whether this is fortuitous or due to special geological conditions. This paper points out the main physical and chemical conditions that are necessary to start and to sustain fission reactions in a natural environment and tries to show that most of these conditions are related to the age of the uranium deposits.

Beside uranium deposits, the Franceville basin contains one of the largest Mn-deposits in the world, namely the Moanda deposit. Reserves of the Moanda deposits are estimated to be 200 Mt of Mn at concentrations up to 48%. This deposit has been formed by a 'lateritic' alteration process of the Francevillian black shales which contain Mn-bearing carbonates.

The early Proterozoic is considered as one of the main periods for Mn deposit formation. In the early Archean it is presumed by Roy (2000) that 'Fe²⁺ and Mn²⁺ in solution were separated by preferential precipitation of the former and the retention of the latter in dissolved state'. Precipitation of Mn first happened at a very large scale 2.3–2.1 Ga ago in the Paleoproterozoic Kalahari manganese deposit (Transvaal Supergroup, South Africa). Whether this dissociation is related to the

variation of dissolved oxygen in the marine environments during transgression–regression episodes or is due to hydrothermal exhalations is still controversial (Glasby, 1997; Roy, 1992, 2000; Klemm, 2000). The study of the Moanda deposit allows a better understanding of the relations between the geochemistry of Fe and Mn, the evolution of the composition of atmosphere and the paleogeography of the basins at that time.

The relation between Proterozoic Mn deposits and black shales has been recognized by various authors e.g. in the Azul (Bernardelli and Beisiegel, 1978; Beauvais, 1984) and Amapa deposits of Brazil, and the Tangganshan deposit of China (Roy, 1992). The period between 1950 and 2100 Ma was generally favourable for the deposition of organic-rich sediments and Condie et al. (2001) have inventoried ten basins worldwide where the thickness of black shales sediments range between 150 and 2000 m. This period of black shale deposition is interpreted as recording the break-up of supercontinents resulting in increased numbers of partially closed marine basins with consequent disruption of ocean currents and increased ocean ridge activity, collectively leading to widespread anoxia (Condie et al., 2001). It will be shown here that the differences in carbon isotopic compositions of organic matter of the Francevillian black shales reflect oxic and anoxic environments and provide information on the oxygen concentration of the atmosphere during their deposition.

The present study tries attempts to connect the above observations in order to show that the formation of the Mn and U deposits and the occurrence of nuclear fission reactions are related to the evolution of the composition of the atmosphere between the time of deposition of the Francevillian sediments and their diagenesis, that is between circa 2150 and 1950 Ma ago. For this, we will refer to several models that have been

proposed to explain the formation of the manganese and uranium deposits and of the fission reactors which are already published. However, we shall present only the major points of the arguments that sustain these models. The focus is to show the relationships between the evolution of the Proterozoic atmosphere and the geochemistry of U and Mn.

2. Geological background

The non metamorphic Francevillian Series outcrops in three different intracratonic basins (Fig. 1): the Plateau des Abeilles, the Franceville and the Lastoursville basins. These basins represent the continental platform of a more distal basin, the basin of Okondja. The lower formation of the

Okondja basin contains basic volcanic rocks (peridotites, basalts, spilites and basaltic tuff) forming greenstones that represent the oceanic crust of an aborted ocean (Weber, 1968; Ledru et al., 1989). The mined Mn and U deposits are all located in the Franceville basin and only this basin will be described here.

The stratigraphic column of the Franceville basin has been subdivided by Weber (1968) into five formations named from bottom to top FA to FE (Fig. 2).

2.1. The FA formation

This formation increases from 100 to 1000 meters in thickness from the edge to the central part of the basin; it contains all the uranium deposits. It consists of fluvatile conglomerates and

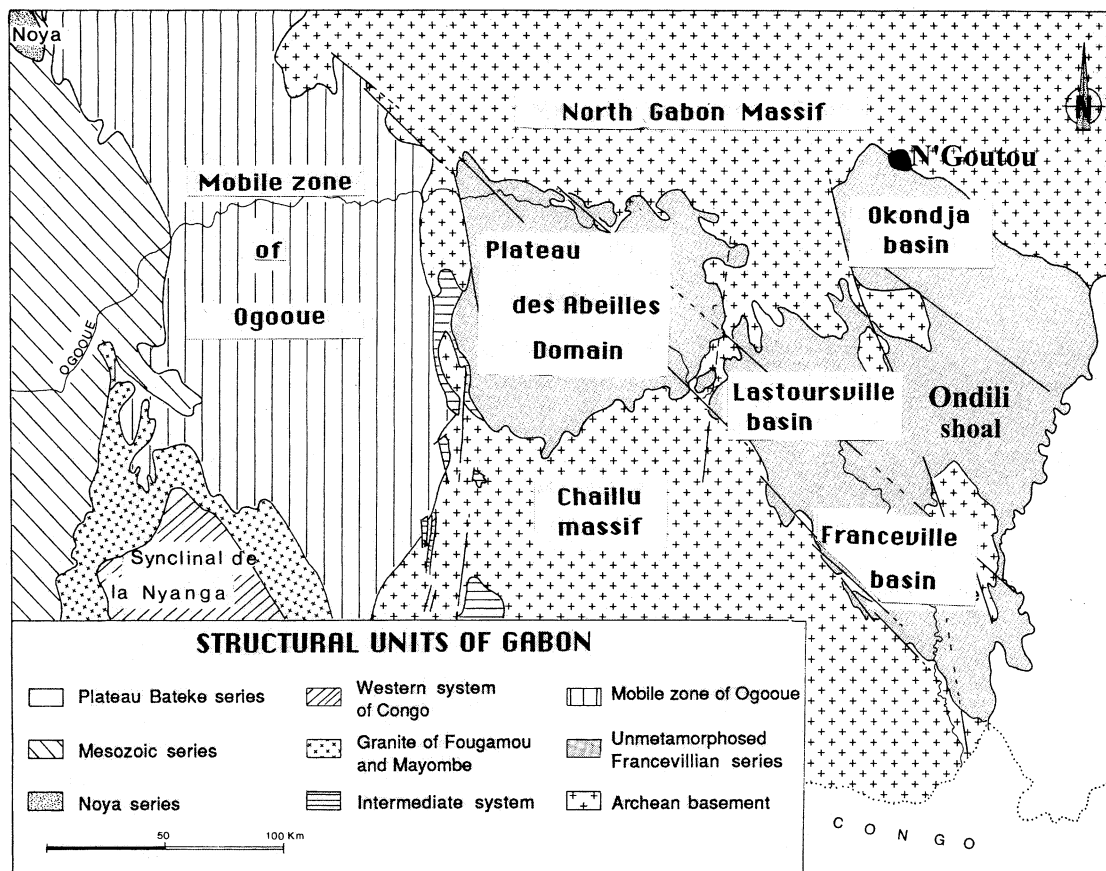


Fig. 1. Schematic structural map of the Francevillian basins.

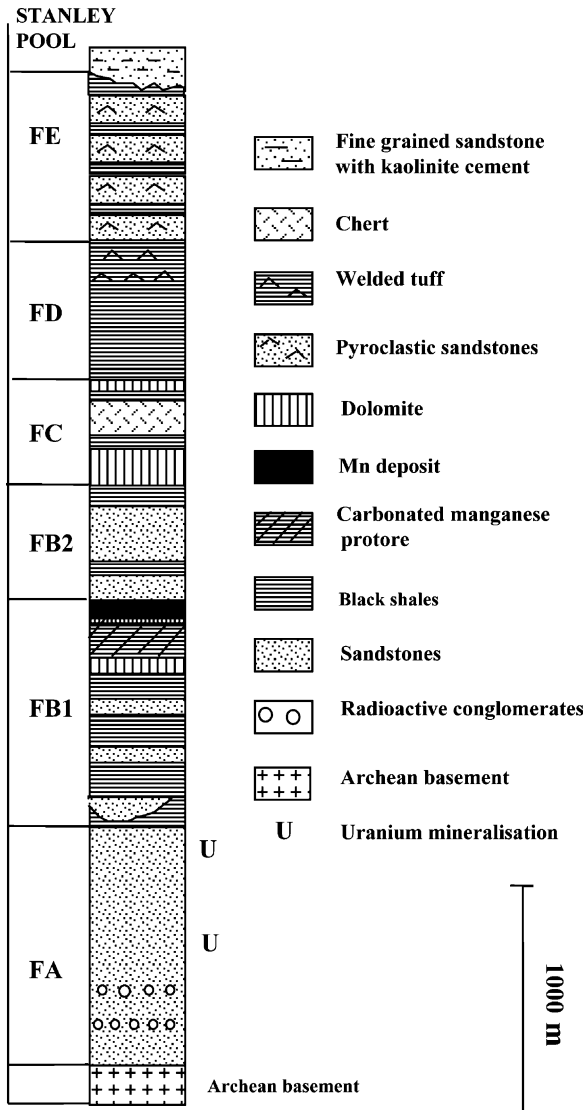


Fig. 2. Stratigraphic column of the Francevillian Series in the Franceville basin.

coarse to medium-grained, poor-sorted sandstones overlain by marine well-sorted sandstones deposited in tidal to supratidal environments. Coarse, medium and fine-grained sediments form sequences of large horizontal extent. The FA sandstones of the Franceville basin are made of very mature material suggesting that they were affected by many cycles of erosion-sedimentation. Such multi-cycles allowed the formation of heavy

mineral deposits in sedimentological settings such as fluvial placers. At Oklo, the mineralised sandstones (the uppermost 10 meters of the FA Formation) were deposited in a tidal environment of beaches and very large, wide, tidal bars in which coarse, well-sorted sandstones alternate with micaceous, fine-grained sandstones (Deynoux et al., 1993).

The FA sandstones consist mainly of quartz, muscovite, more or less altered biotites and feldspars (mostly microcline), abundant in the lower fluvial sandstones but rare in the overlying marine sandstones. Heavy minerals such as zircon, thorite and monazite are abundant in conglomerates and coarse sandstones. Types of matrix and cement determine the colour of the sandstone, but it must be noted that well-sorted marine sandstones at the top of the FA formation were cemented by an intense silicification event. Three facies occur in a sequence of red-, green- and black-coloured sediments (Gauthier-Lafaye and Weber, 1989). The contact between sediments of different colour is clearly discordant on the bedding, which indicates that the coloration is not of sedimentary origin but was acquired during the diagenetic stage.

The red colour is due to hematite impregnation of the argillaceous matrix; hematite also surrounds the quartz grains between their detrital boundaries and their overgrowth. The argillaceous matrix consists mainly of illite. Ancient detrital biotites and heavy minerals such as monazites and zircons (Mathieu et al., 2000) are highly altered. Biotites are opaque due to the occurrence of fine hematite and titanium oxides inclusions on their surface and have now a muscovite composition. The detrital monazites are altered to a Th-OH silicate with very low concentrations of U and REE, whereas altered zircons show several growth zones enriched in REE, P, Th and U (with Th/U = 5–10) (Mathieu et al., 2000). These red-coloured sediments may contain dolomite and sulfates (anhydrite, gypsum and accessory barite) in the fluvial and tidal environments.

Black sandstones are restricted to the higher levels of the FA formation. Their colour is mainly due to organic matter in pore spaces. This organic matter consists of solidified petroleum (pyrobitu-

men) that fills the primary and the secondary porosity of the sandstones and the fractures (Gauthier-Lafaye and Weber, 1981; Gauthier-Lafaye, 1986; Cortial et al., 1990; Nagy et al., 1991, 1993). In the primary porosity, organic matter occurs around detrital quartz grains or is trapped in quartz overgrowth. There are two types of black sandstones depending on the alteration of the detrital biotites. The first type contains weakly altered biotites of composition intermediate between biotite and chlorite. The matrix consists mainly of iron-rich chlorite. In the second type of black sandstone, the detrital biotites are altered to a pale colour and resemble muscovites with titanium oxides on their surface. The matrix consists of illite without chlorite and the black colour is due the presence of organic matter in secondary porosity. The first type of black sandstone is interpreted as sediments that were never oxidised, whereas the second type corresponds to sediments which were first oxidised and then reduced by fluids associated with oil migrations.

Green sediments are usually located between the red and the black sandstones. They contain highly altered biotites, which look like 'sandwiches' made of flakes of muscovite and green iron-rich chlorite. The matrix contains both illite and green iron-rich chlorite in varying proportions. In some sandstones, hematite rims remain between the quartz boundary and the quartz overgrowth suggesting that these sediments were originally oxidised. Pyrite accumulations are common in these green sandstones. Pyrite corrodes both the detrital quartz and their overgrowths, and is usually associated with green chlorite. These pyrite accumulations are interpreted as reduced fronts resulting from the flow of reducing fluids through oxidised sediments.

2.2. The FB formation

Following the subsidence of the FA basin, the ocean invaded a large area, the limits of which are unknown. Towards the northeast, the Franceville basin was separated from the deepest Francevillian basin, namely the Okondja Basin, by the shoal of Ondili.

The FB Formation is composed chiefly of black shales, forming a 400–1000 meters thick unit. The black shales are characterized by considerable concentrations of organic matter (C_{org} up to 15%, Gauthier-Lafaye and Weber, 1989). The deposition of these black shales may have occurred during a worldwide black shale event (Shunga event of Melezhik et al., 1999) between approximately 1.9 and 2.05 Ga. This event is related to the stromatolite explosion (Semikhatov and Raaben, 1994; Melezhik et al., 1997). Indeed stromatolites are well preserved in the FC cherts (see next section).

At the edges of the basin, the bottom of this formation consists of olistoliths and polygenic breccias resulting from the collapse of the underlying units into the basin. In the black shales, transgression–regression episodes are marked by the occurrence of thin layers of dolomite and sandstone. These interlayered levels are more abundant at the edge of the Franceville basin than in its more central parts (Fig. 3).

The detrital minerals occurring in the black shales are mainly quartz, feldspars, muscovite and biotite. The matrix consists largely of organic matter which consists of a homogeneous phase concentrated in thin layers parallel to the bedding (Gauthier-Lafaye and Weber, 1981; Mossman et al., 1993), clays (illite and chlorite), Ca, Mg, Fe and Mn-carbonates and pyrite. The Fe-carbonates and pyrite are more frequent at the base and the middle of the formation. In some 5–10 m thick carbonated layers, Fe content may reach 40% and form so-called iron formations. The amount of Mn-carbonates increases near the top of the formation where they form the protore of the manganese deposits (Weber, 1968, 1997) as described in a later section.

The uranium content of the FB-black shales ranges between 3.5 ppm (average of 48 samples in Gauthier-Lafaye, 1986) and 10.8 (average of 6 samples in Mossman et al., 1998). These values are particularly low when compared to black shales from different basins of various ages compiled by Vine and Tourtelot (1977), which have an average uranium content of 30 ppm, and to the USGS Standard Devonian Oil Shale which has an uranium content of 48.8 ppm.

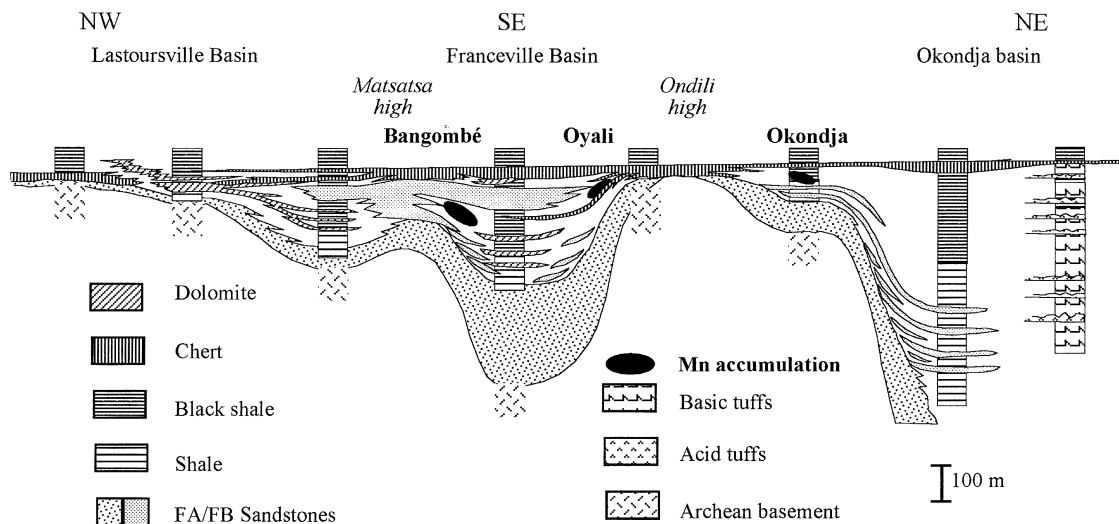


Fig. 3. Schematic palaeogeographic cross-section of the Francevillian sub-basins and location of the Mn ore deposits.

2.3. FC formation

This 10–40 m thick formation consists chiefly of massive dolomite and thick-banded cherts. Stromatolites, together with organic mats, are well developed in cherts and are described in detail by [Bertrand-Sarfati and Potin \(1994\)](#). The cherts contain several filamentous and circular forms, 40–100 microns in diameter, forming colonies that might be microbial ([Mossman et al., in press](#)). Dolomites and cherts resulted from dolomitisation and silicification of previous calcitic or Mg-calcitic stromatolites, but microscopic stromatolitic structures are better preserved in cherts than in dolomites. The FC Formation is not synchronous in the Franceville basin. At the edge of the basins and on shelves, stromatolites first appear in the FB black shales. In the central part of the Franceville basin, the FC unit occurs after the FB black shales and corresponds to a quasi-emersion episode which is preceded by a marine littoral unit represented by kilometers long sand shoal bars (FB2a).

2.4. FD–FE formations

The FD Formation consists of black shales, with ignimbrite tuff dominant at the top of the

formation. The FE Formation comprises epiclastic sandstones and interlayered shales. The FD–FE Formations are more than 1000 m thick in the Franceville basin. These formations are probably thicker in the northern part of the Okondja Basin, but this forested area is poorly known.

In the FD–FE Formations of the Franceville basin, black shales remain the dominant sediments, but unlike the FB Formation, they contain no Mn accumulations. However, Cu enrichments occur at the bottom of the FD Formation. This is due to the change in the volcanic activity, which became acidic as compared to the basic volcanism in the FB Formation. This evolution is related to the occurrence of two major phases affecting the Archean Congo-Sao Francisco craton ([Feybesse et al., 1998](#)): (1) the opening of the Franceville basin during the FA and FB deposition in a pre-oceanic setting, and (2) the opening of an intracontinental rift during the deposition of the overlying formations.

2.5. Intrusions, deformations and late evolution

An intrusion of alkaline rocks, the N'Goutou complex, occurs at the edge of the Okondja basin. This intrusion is interlayered in the sediments of the base of FB Formation. The N'goutou volcanic

complex has been dated by Rb–Sr measurements on syenites and pegmatites. An isochron gives an age of 2143 ± 143 Ma (Bonhomme et al. 1982).

Later dykes of dolerite intrude the overall Francevillian series in the Franceville basin forming two orthogonal systems oriented NNW–SSE and ENE–WSW. These dolerites were dated by K–Ar method on feldspathic fractions giving an age of 970 ± 30 Ma (Bonhomme et al., 1982).

In the Franceville basin the succession is only slightly deformed. Maximum deformation occurs in rocks affected by synsedimentary faults activated during a later compressive tectonic episode. In the Okondja Basin the deformations are more intense, and the succession is weakly folded. Thereafter, the basin remained remarkably stable until recent uplift resulting in its erosion under the present weathering regime.

2.6. Diagenesis

The highest diagenetic level reached by the sediments corresponds to the level defined as very low grade metamorphism characterized by crystallization of chlorite and illite, mainly of 1M polytype (Gauthier-Lafaye, 1986). Only at the bottom of the FA Formation 2M-illite may have some importance. In the iron formation, greenalite and stilpnomelane occur. The persistence of greenalite without minnesotaite or grunerite also indicates a minimal metamorphic grade. Fluid inclusion studies of quartz overgrowths and carbonate cements indicate that the maximum temperature reached in the Franceville basin during diagenesis ranges between 180 and 200 °C at a maximum pressure of 1000 ± 200 bars (Gauthier-Lafaye and Weber, 1981; Gauthier-Lafaye and Weber 1989; Savary and Pagel, 1995; Mathieu, 1999). These fluids are highly saline brines (28.7 wt.% NaCl eq. to 30 wt.% CaCl₂ eq.), rich in Li, Br and SO₄ (Mathieu et al., 2000). Optical and electron microscopic properties and chemical compositions of organic matter have been described in detail by Cortial et al. 1990; Nagy et al., 1993; Mossman et al., 1993, 1998.

Organic matter of the Francevillian Series has experienced high levels of thermal maturity: H/C and O/C ratios are low and the ‘coke’ stage has

been reached. The true anthracite stage, which is defined by transmitted electron microscopy (TEM) has not been detected, thus suggesting the absence of metamorphism (Cortial et al. 1990).

The reservoir rock of the FA formation only contains migrated solid bitumen, of two types according to their uranium content: (1) barren bitumens are located in the primary porosity of the sandstone, and exhibit high reflectance ($R = 4\%$), ranging from 800–5000 Å and local molecular orientation (LMO), under TEM; (2) mineralized bitumens have a low reflectance (R ranging from 0.4 to 2.6%) and present no or little LMO as a result of intense oxidation.

The main source for these migrated bitumens has been identified as the black shales of the FB Formation which were sometimes placed below the FA reservoir by normal faults. In the upper part of the FA Formation, interlayered shales with very high organic carbon content may also have served as source rocks. The possible source kerogen is ‘sapropelic coal’ with R ranging between 5 and 7% and LMO values ranging between 150 and 300 Å. Hydrocarbons were generated when sediments of the FB formation passed through the oil window (Gauthier-Lafaye, 1986; Mossman, 2001).

2.7. Radiometric ages

The Francevillian Series and the geological events that affected the sediments have been dated by several geochronometers. The following ages were obtained:

The deposition of the FB black shales has been dated by Rb–Sr measurements on interlayered syenites of the N’goutou volcanic complex (2143 ± 143 Ma) by Bonhomme et al., 1982.

The time of petroleum generation in the Franceville basin has been dated by two Sm–Nd isochrons on small authigenic clay fractions of the FB Formation. These give ages of 2099 ± 115 and 2036 ± 79 Ma (Bros et al., 1992; Stille et al., 1993) which are in good agreement with Pb–Pb dating of authigenic clay fractions of the FB black shales (Gauthier-Lafaye et al., 1996a).

The age of the uranium deposit is 2050 ± 30 Ma as determined by using classical U–Pb methods on uraninites (Gancarz, 1978). By comparing the

fluence of the fission reaction to the amount of fission elements (mainly REE) produced it is possible to determine the date of the fission reaction with a great precision. The result gives an age of 1950 ± 40 Ma (Ruffenach, 1978, 1979; Holliger, 1988; Naudet, 1991).

Late diagenesis has been dated from clay fractions from the FB Formation using the Rb–Sr method yielding an age of 1870 ± 50 Ma (Bonhomme et al., 1982).

The dolerite dykes were dated by the K–Ar method at $970 \text{ Ma} \pm 30 \text{ Ma}$ (Bonhomme et al., 1982).

The time of basin uplift is unknown. The only radiometric data available is a U–Th age of $76\,500 \pm 6800$ years obtained on secondary torbernite related to the weathering of the Bangombé uranium deposit (Bros et al., 2000).

3. The manganese deposits

In the Franceville basin, manganese forms two main deposits that are located at the top of two plateaus (Fig. 5): Bangombé (40 km^2) and Okouma (13 km^2). The Mn ore consists of Mn oxides, mostly pyrolusite, cryptomelane and nsutite with minor manganite at the bottom, rams-

dellite and lithiophorite at the top. According to Weber (1997), these Mn deposits resulted from a lateritic alteration of a Mn-carbonate ‘protore’ which is observed only in drill cores.

Mn accumulations occur in the FB and FC formations. However, all major Mn accumulations are located at the top of the FB1 formation and were formed at the margin of a shallow shelf. The deposits of Bangombé and Okouma are situated at the edge of the Franceville basin whereas the smaller Mn-accumulations of Oyali and Okondja are located at the edges of the Ondili shelf (Fig. 3).

3.1. Description of the protore of the manganese deposits

The so-called manganese protore in the upper 100 m of the FB Formation is enriched in Mn-carbonate (5–30% Mn) compared to the underlying black shales which contain $< 1\%$ Mn but are enriched in dolomite. This 30–80 m thick manganese horizon consists mainly of Mn-carbonate-bearing black shales with intercalations of Mn-poor sandstones, dolomitic or sandy-dolomitic sediments. The Mn-bearing mineral is a triple carbonate of manganese, calcium and magnesium with Mn and Ca dominant over Mg. The MnCO_3 molecular proportion in the carbonate is generally up to 40–70% in the shales and from 10 to 50% in the interlayered fine-grained sandstones. These Mn-carbonates have commonly replaced nearly pure dolomite suggesting that they were formed later, during diagenesis (Azzibrouck-Azziley, 1986; Weber, 1997).

The Mn anomaly in the black shales is associated with a significant anomaly of transition-metals such as Co, Ni and Cu. In Mn black shales, the concentrations of these elements are respectively 20, 5, and 3 times higher than in the non-manganiferous black shales whereas the Mn has been enriched 70–80 times. Despite their location in sulfides, mainly pyrite, these elements are positively correlated with Mn but negatively correlated with Fe (Weber, 1997). This suggests a common volcanic or hydrothermal origin.

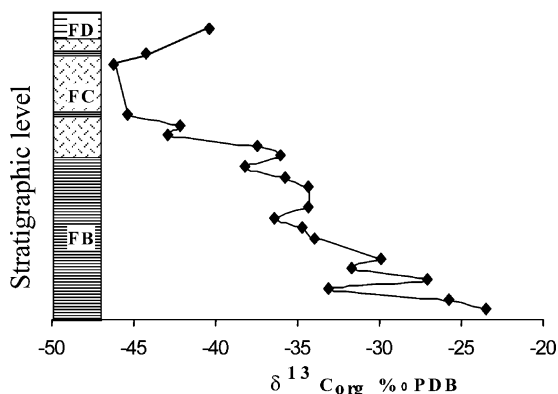


Fig. 4. Distribution of $\delta^{13}\text{C}_{\text{org}}$ in the Franceville formation. Analysis were performed at the Max-Planck Institute, Mainz and at the Centre de Géochimie de la Surface, Strasbourg.

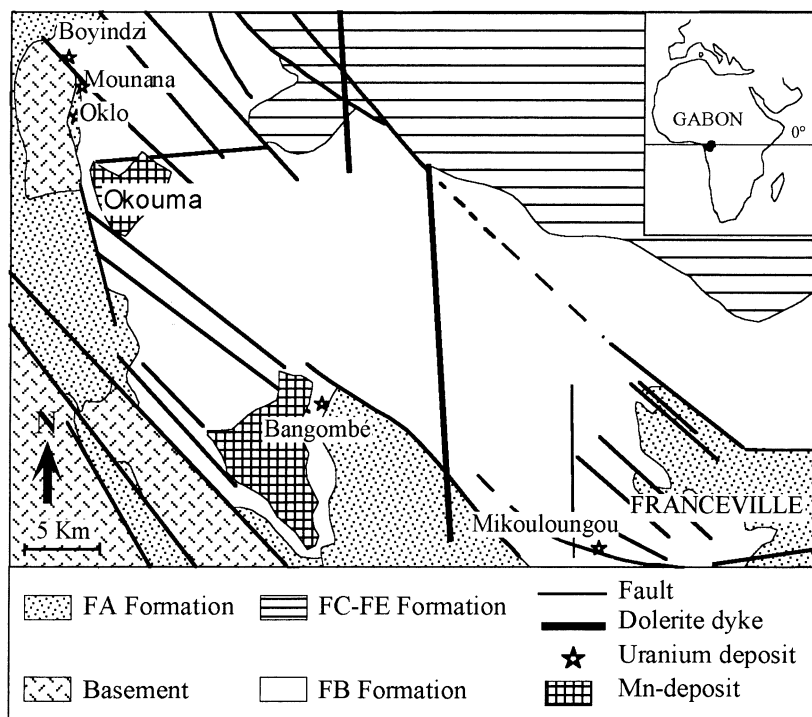


Fig. 5. Schematic geological map of the Franceville basin and location of the Mn and U ore deposits.

3.2. The iron formation

In the Okouma plateau a 8–10 m thick ‘iron formation’ occurs under the manganiferous horizon. In other plateaus (i.e. Bangombé) only slight iron-enrichments occur at the base of the manganiferous horizon with some recurrences within the Mn-protore.

This ‘iron formation’ consists of millimeter to centimeter scale interbedding of cherts, phosphate-rich layers, and iron-rich shales. Iron is concentrated in three different types of rocks depending on the dominant iron-bearing minerals: sulfide rich shales with dominant pyrite, carbonated rocks with siderite, and silicate sediments with dominant greenalite and minor stilpnomelane. In addition to the high iron content (25–35% Fe), the ferruginous horizon is characterized by a low Al content (< 1%) and a high P content (> 1%). Phosphorus content is even higher in the Fe-bearing layers than in Mn-black shales where P content is already

three to four times higher than in normal black shales.

4. The uranium deposits

The Franceville basin contains five uranium deposits. From North to South (Fig. 5) these are Mounana, first to be discovered in 1956, Boyindzi, Oklo-Okelobondo, Bangombé and Mikouloungou. The Oklo-Okelobondo and Bangombé deposits contain the famous natural fission reactors. These deposits have been mined out with the exception of the Bangombé deposit. Altogether these deposits supplied 28 000 tons of uranium mined from 1961 to 1999.

The uranium deposits of the Franceville basin are located in the upper part of the FA Formation and are associated with tectonic structures which formed traps for hydrocarbons. Mineralized layers are coarse-grained and well-sorted tidal to supra-

tidal sandstones. The matrix is mainly secondary quartz, clay being a minor phase. In the non-weathered ore most of the uranium is in the form of uraninite and coffinite, which are closely associated with migrated hydrocarbons occupying secondary porosity of the sandstones. The mineralized organic matter consists of solid pyrobitumen with an atomic hydrogen/carbon ratio lower than 0.5 (Cortial et al., 1989).

Uranium is associated with calcium, vanadium, iron, lead, barium, zinc, copper and molybdenum. Up to 6% calcium is disseminated in uranium-bearing minerals (uraninite). Vanadium content was very high (0.01–1%) at Mounana, Boyindzi and Mikouloungou. At Mounana, V was economically exploited with vanadium oxides (karelianite, montroseite, duttonite, corvusite) and silicate (roscoelite) occurring in the non-weathered ores, whereas uranium, lead and barium vanadates occurred in the weathered zones. In the ores of high uranium content, hematite and sulfides such as pyrite, marcasite and melnikovite may have some importance. Lead is of radiogenic origin and is mainly concentrated in galena. Minium and even native lead have locally been found but only in the fission reactors. Zn, Cu and Mo are present in minor concentrations. They occur as sulfides (blende, chalcopyrite, chalcocite etc.) or sulfates (in the weathered zones) and wulfenite. Barite is a common accessory mineral except in the vanadium-rich zones.

When uranium is located inside organic matter, the uranium content of the ore ranges from 0.1 to 1%. The uranium is then associated with sulphides, mainly pyrite, chlorites and calcite. $\delta^{13}\text{C}$ of this calcite is low (–10 to –15%) suggesting that part of its carbon has an organic origin. Barren calcite outside the deposits has a $\delta^{13}\text{C}$ value of 0 to –5%. In ores with a high uranium content (1–10%), uraninite is associated with hematite, and illite. This type of ore is located in highly fractured rocks. Ore transitional between these two types exists. This suggests that both types of uranium ores are products of the same oxidation–reduction process and that the highly fractured zones have been more permeated by the oxidized uranium-bearing fluids.

5. The natural nuclear fission reactors

5.1. Description of the reactors

Fifteen natural nuclear fission reactors (hereafter reactors) were discovered in two uranium deposits of the Franceville basin. Fourteen are located in the Oklo-Okelobondo deposit and one in the small deposit of Bangombé which is 30 km from Oklo-Okelobondo. All the reactors of Oklo-Okelobondo have been mined out or are no longer accessible because the open pit and underground mines have been flooded. The reactor of Bangombé, which is the smallest, has been preserved together with its host uranium deposit for further scientific studies of the behaviour of fission products and actinides in a geological environment. The Bangombé reactor is located very close to the surface (12 m deep for Bangombé and 100–260 m for the Oklo-Okelobondo reactors) and is therefore much more affected by weathering than the others. Extensive geological, mineralogical and geochemical descriptions of the reactors are given by Gauthier-Lafaye (1986), Gauthier-Lafaye et al. (1989, 1996b) and in a report that synthesised the results obtained during a recent European program (Oklo-Natural Analogue: phase II, 1996–1999) studying the behaviour of fission products in the water-rock systems of the various reactors (Gauthier-Lafaye et al., 2000). Other major contributions are reported in the proceedings of two IAEA international conferences held in Libreville (1975) and Paris (1978) and in the final report of the European program ‘Oklo-Natural Analogue: phase I’ (Blanc, 1996).

A typical reactor is shown in Fig. 6 (reactor 9). The size of the reactors is quite variable. The biggest reactor (reactor 2) is a 12 m long, 18 m deep and 20–50 cm thick lens. At Bangombé the reactor is only 5 m long, 1 m wide and a few centimetres thick, but recent weathering has dissolved a large part of this reactor (Gauthier-Lafaye et al., 2000).

The reactor cores consist of a 5–20 cm thick layer of uraninite embedded in clays (illite and chlorites). The uranium content of the core ranges between 40 and 60%. Accessory minerals are mainly sulphides (pyrite and galena), hematite

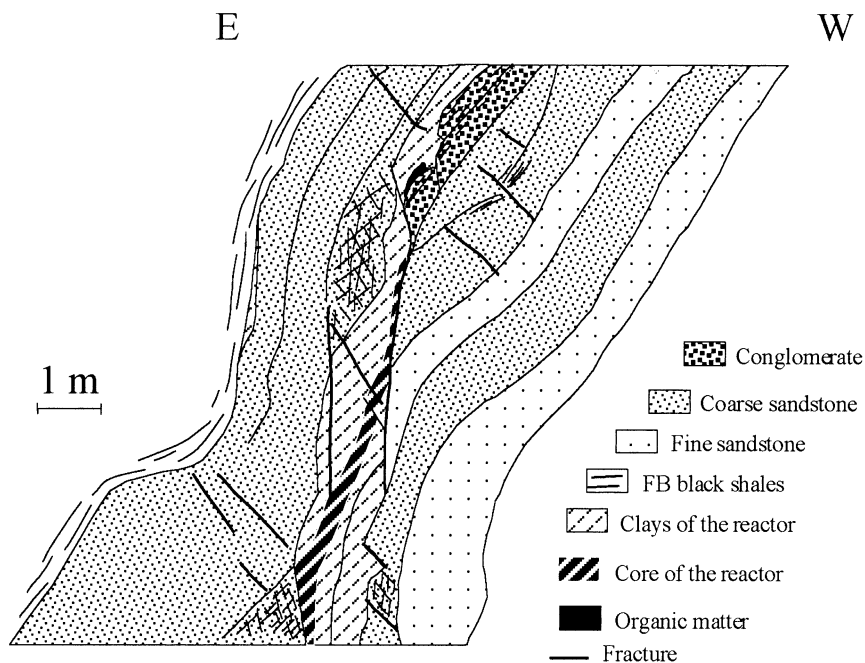


Fig. 6. Cross section of reactor 9 (150 m depth), at the Oklo uranium deposit.

and phosphates (mainly hydroxyapatite). The clay minerals reflect the thermal gradient during the operation of the reactors (Gauthier-Lafaye et al., 1989; Pourcelot and Gauthier-Lafaye, 1999), with Mg-chlorite and 2M1-illite close to the core and 1M-illite and Fe-chlorite at the edge. In some cases, quartz grains, more or less altered and dissolved, remain in the clays.

5.2. Fission reactions

Fission reactions started in high grade uranium ore when the uranium content of the sandstones reached 10% (Naudet, 1991). Once fission reactions began, the temperature in the reactor core increased, starting a convective hydrothermal system around the reactor. Core temperatures reached 400 °C (Gauthier-Lafaye et al., 1989; Mathieu et al., 2000) and decreased rapidly towards the edges (thermal gradient around 100 °C/m) with heat transferred largely by con-

duction (Gerard, 1997; Gerard et al. 1997). Hydrothermal circulation caused the dissolution and migration of 80% of the silica from the mineralised sandstones. This decreased the volume of the sandstones and increased the uranium content of the residual layer which then consisted mainly of clays and uranium dioxides. Furthermore, it is been shown that in the reactor 2, the hydrothermal circulation has introduced 50% of the present uranium content. Such processes allowed a five fold increase in the amount of uranium per unit volume, forming the reactor core (Gauthier-Lafaye et al., 1989).

The hydrothermal fluids produced by the fission reactions were similar to the diagenetic fluids (Mathieu et al., 2000) but their temperatures, as measured in fluid inclusions, were higher, ranging from 280 to 420 °C (Mathieu, 1999). They also contained traces of CH₄, CO₂, O₂, H₂ and H₂O₂ (Dubessy et al., 1988; Mathieu et al., 2000), with the later three species resulting from the radiolysis

of water in the core of the reactor. Because H_2 diffuses faster than O_2 , very oxidized conditions could have occurred in the reactors, accounting for the precipitation of minium (Pb_3O_4) which needs a high oxidation potential and very low S content in the hydrothermal fluids. During the fission reaction, methane and CO_2 were released from organic matter at high temperatures (Mathieu et al., 2000). Uraninite depleted in ^{235}U occurs in bitumen nodules suggesting that organic matter was still mobile during the fission reactions (Nagy et al., 1993).

In order to start and sustain a fission reaction, the concentration of neutron ‘poisons’ in the system must be low (Naudet, 1991). In geological systems B, V and REE are the most important poisons. Differences in the V concentration of the various deposits in the Franceville basin may explain the distribution of the reactors. The deposits of Mounana, Boyindzi and Mikoulougou have a high V content and no reactors. The concentration of B and REE is low in all of the uranium deposits. For B, this is due to the meteoric origin of the mineralising fluids, which did not migrate through the basement, a common source of this element. Because at least part of the uranium was released by the leaching of detrital monazites (see later section), the REE were fractionated from U during the migration of uranium from the conglomerates to the deposits. This fractionation may be due to differences in pH-Eh conditions for the dissolution and precipitation of REE and U. Mathieu et al. (2000) has calculated that 435×10^6 tons of REE were leached from monazites and mobilised in the Franceville basin, but no trace of these REE has ever been found, suggesting that conditions were not favourable for their precipitation and concentration in the basin. However, Hidaka and Gauthier-Lafaye (2000) have shown that in some Oklo uraninites located far from the reactors, the neutron fluence recorded in REE is in excess of the spontaneous fission-released neutron fluence (due to ^{238}U), which suggests that fission reactions began in these samples, but could not be sustained because the REE content was too high.

6. Evolution of the atmosphere as recorded by $\delta^{13}C_{org}$

Carbon isotopic analyses have been performed on total organic carbon of black shales. Because all analysed organic materials have H/C ratios lower than 0.5 (Cortial et al., 1990), it is considered that their $\delta^{13}C$ values are close to the value of their respective kerogens. Most of the samples were obtained far from the uranium deposits and the natural reactors. Therefore, samples were not subjected to any radiolytic phenomena that could have an effect on their carbon isotopic compositions.

From the bottom of the FB Formation to the overlying FC and FD Formations, $\delta^{13}C$ of organic matter decreases from about -23% to about -45% (minimum -46.2%) (Fig. 4). The lowest values are located in black shales associated with cherts and dolomites deposited in shelves and at the edges of the Franceville basin, whereas the highest values correspond to black shales at the bottom of the FB Formation in the central part of the basin, or to pyrobitumen of the top of the FA Formation.

The $\delta^{13}C$ values of the Fe and Mn-carbonates of the FB black shales range between $+0.7$ and -13.4% PDB whereas the $\delta^{13}C$ values of dolomites range between 2.6 and 6.3% .

The $\delta^{13}C$ of marine organic matter is mainly dependent on the isotopic discrimination between ^{12}C and ^{13}C associated with the biological fixation of CO_2 . During the past 3.5 Ga, photosynthesis has been the major process that controls the isotopic composition of carbon resulting in a nearly constant $\delta^{13}C_{org}$ value of $-25 \pm 10\%$ (Des Marais, 1997; Schidlowski, 2001). However, in late Archean to early Proterozoic sediments, $\delta^{13}C$ values as low as -65% have been measured (Des Marais, 1997). Such low values reflect particular processes that can enrich organic matter in ^{12}C . In the 2.0 Ga old Zaonezhskaya Formation (NW Russia), Melezhik et al., (1999) report similarly low $\delta^{13}C_{org}$ values in shungite with a similar trend in the stratigraphic column. Such low values were interpreted as the result of diagenetic, catagenic and metamorphic alterations (Melezhik et al., 1999). However, this interpretation cannot be

applied to the organic matter of the Franceville basin because it never reached such high degree of metamorphism. It is therefore suggested that very low $\delta^{13}\text{C}_{\text{org}}$ values result because already ^{12}C -enriched organic carbon is used by anaerobic, methanotrophic and/or methylotrophic microbes (Hayes, 1994; Des Marais, 1997; Klemm, 2000; Schidlowski, 2001). By fermentation, methanogenic organisms produce CH_4 with very low $\delta^{13}\text{C}$ which in turn may be used by methanotrophic organisms to produce organic matter further depleted in ^{13}C . The resulting $\delta^{13}\text{C}$ of the organic residue in sediments thus depends on the extent to which fermentation by methanogenic bacteria, consumption of CH_4 by methanotrophic organisms and consumption of CO_2 by photosynthetic organisms operate to control the carbon isotopic geochemistry (Hayes, 1994). Hayes (1994) reports that in some late Archean series 'isotopic signals of methanotrophy appear first and most strongly in stromatolitic units' and he interprets this fact as follow: 'if O_2 were the trace gas and CH_4 globally distributed, methanotrophs have grown in close proximity to oxygenic algae, because it was only there that supplies of O_2 were adequate'. Because a similar observation is made in the FB–FC formations it is suggested that the measured low $\delta^{13}\text{C}$ values are related to the up filling of the basin and its quasi-emersion occurring during the stromatolites-rich FC cherts and dolomites deposition. The low $\delta^{13}\text{C}$ values in the FB black shales also suggest that at those times the atmosphere probably had much less O_2 than at present (Hayes, 1994).

7. Formation of the protore of the Mn deposit

It has been suggested that the volcanic and hydrothermal activity in the surrounding Okondja basin supplied for Mn and Fe to the seawater (Weber, 1968). However, at this time (≈ 2.1 Ga), Mn content of the ocean water was probably very high and with high Mn/Fe ratio. Indeed, during the late Archean and early Proterozoic many large iron deposits occurred but conditions for manganese precipitation were normally not achieved (Roy, 2000). The reducing conditions in the major part of the FB basin and especially in the deeper

zones allowed the migration of Mn and Fe over great distances. CH_4 production by methanogenic archaea as suggested by carbon isotopic data sustained such reducing conditions throughout the Francevillian Basin.

The ability of Mn oxides to scavenge transition elements, especially Co, Ni and Cu, is well known, particularly in present-day oceanic nodules. The apparent paradox that Co, Ni and Cu are strongly correlated with Mn in the Franceville basin but occur in different minerals, principally pyrite, could be explained by initial precipitation of these elements as oxides and their later diagenetic reduction to respectively, sulphides and carbonates. The low $\delta^{13}\text{C}$ of the Fe and Mn-carbonates compared to the dolomites suggest a more important organic carbon contribution to the manganese and iron carbonates than to the dolomites.

The precipitation of Mn oxides during the deposition of black shales has been described by Huckried and Meischner (1996) for modern black shales of the Baltic Sea and by Manikyamba and Naqvi (1995) who suggested a similar model for the formation of the Archean Fe–Mn formation of the Sandur schist belt (India). In their model, the formation of carbonates or oxides depends strongly on the O_2 and CO_2 concentrations in the water, which in turn depends on the composition of the atmosphere and on biologic activity in the local environment.

In all deposits, the FB black shales were deposited at the margin of the shallow shelf, where concentrations of dissolved oxygen were high due to the intense biologic activity as it is suggested by the very low $\delta^{13}\text{C}$ values recorded in organic matter (Fig. 7). In these zones, Mn and Fe precipitated first as oxides during the regressive cycles. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ chemocline was reached before the $\text{Mn}^{2+}/\text{Mn}^{4+}$ chemocline, thus, as recorded in the FB black shales, Fe formation is always located below the Mn protore. Nevertheless the Fe accumulations are very small by comparison with the Mn deposits, confirming the high Mn/Fe ratio of the seawater. During the transgressive cycles, these elements were then incorporated into carbonates (Mn-carbonates and siderite), sulfides (pyrite) and silicates (green-

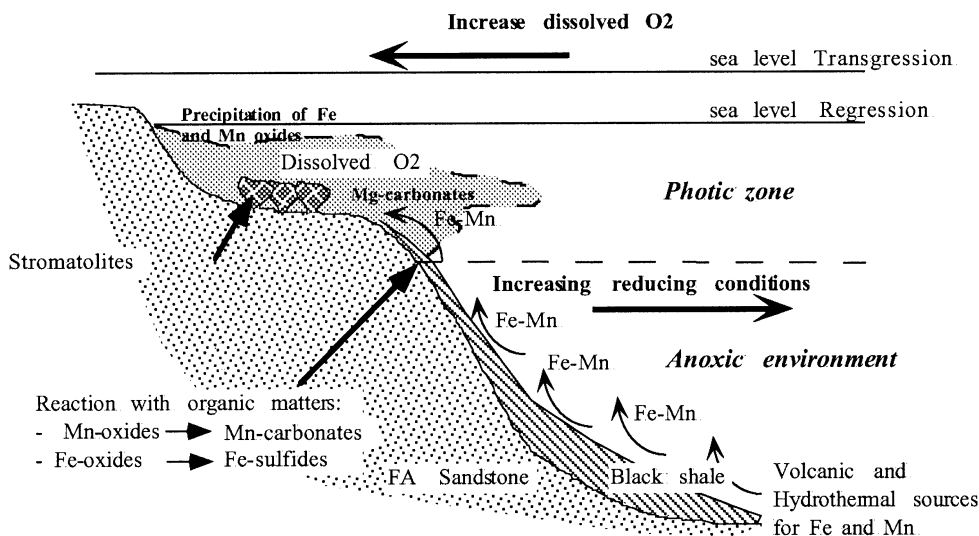


Fig. 7. Model for formation of the manganiferous protore of the Mn ore deposits of the Franceville basin on a marine shelf, during the deposition of the FB black shales. Mn and Fe are sourced in the adjacent Okondja basin.

alite, stilpnomelane) by interaction with the reduced sediments.

8. The change of redox conditions: formation of the uranium deposits

During deposition of the FA sandstones and conglomerates, reducing conditions prevailed as suggested by their mineralogical assemblage (fresh biotite in fine non-oxidised sandstones). Uranium-bearing minerals (monazites, thorites and possibly detrital uraninites) were therefore stable and could have formed deposits similar to the Witwatersrand and Elliot Lake deposits. However, as the burial of the Franceville series progressed, oxygen in the atmosphere evidently increased. This oxygenation of the atmosphere and hydrosphere is recorded by the secondary oxidation of the FA sandstones that occurred during diagenesis and during the oil migration into the FA reservoir. This oxidation event is also responsible for the alteration of the uranium-bearing minerals (monazite and possibly uraninite) and the migration of uranium into the petroleum traps where it met reducing conditions favourable for its precipitation.

In the field the relationship between uranium deposits and oxidation fronts is not conspicuous because these fronts are obscured by the late reduction process. Only at Mikouloungou is the relation obvious and in several places at Oklo where high grade uranium ores are developed in oxidised fractures. Nevertheless, the geochemical association of U with Cu, Mo and V, which often characterises uranium deposits associated with an oxidant front, leaves no doubt of this interpretation. The oxidised uranium-bearing solutions migrated upwards through the lower part of the FA sandstones, which have been oxidised. Uraninite precipitated in tectonic traps when these solutions met hydrocarbons sourced from the FB formation.

Modelling of the fluid flow into the Franceville basin during the formation of the uranium deposits suggests that the oxidised solutions flowed parallel to the longitudinal axis of the basin with preferential pathways at the base of the FA Formation (Salas et al., 2000). In order to maintain the oxidant redox state in the fluids, recharge must have taken place through the FA Formation sandstones cropping out in the Lastoursville basin.

Analysis of the uranium-bearing fluids show that they were very saline waters with concentrations of Ca up to 30% eq. wt.%, Na up to 30 eq.

wt.%. Fluid inclusion entrapment temperatures range from 100 to 170 °C under a pressure ranging between 800 and 1200 bars (Mathieu, 1999; Mathieu et al., 2000). Some fluids are a mixture between brines which equilibrated in the FA sandstone reservoir with carbonate and sulphate minerals and low Na/Ca ratio fluids like those usually accompanying hydrocarbons in petroleum fields (Carpenter et al., 1974). If we assume a concentration of 10 ppb uranium in the solutions, and given that the FA sandstones are 1 km thick and have 10% porosity, one can calculate that 40 000 tons of uranium, the total estimated reserve of the Franceville basin, corresponds to 10 times the water volume contained within the FA sandstone pore space. This suggests that significant water circulation through the FA reservoir was needed to form the uranium deposits and that this water needed to be recharged with O₂ in order to maintain its oxidising potential.

The source of the uranium is believed to be detrital uranium-bearing heavy minerals (including uraninite) which are concentrated in several 100 m thick conglomerates in the lower FA formation (Gauthier-Lafaye, 1986; Gauthier-Lafaye and Weber, 1989). These conglomerates contain monazites and thorites but despite a thorough search of the FA conglomerates for detrital uraninites, this mineral has never been found. This may be because the FA sandstones passed through the oxidation event which would have dissolved any uraninite that was present. That oxidation event allowed the formation of the uranium deposits and the occurrence of fission reactions when a critical mass was reached. Therefore, taking into account the chronology of these phenomena, a considerable increase of the oxygen in the atmosphere evidently occurred between deposition of sediments and formation of uranium ore deposits. This happened between 2.14 ± 14 Ga and 1.950 ± 40 Ga. Unfortunately, the large uncertainty in the radiometric data does not allow us to fix the age of the transition stage more precisely. Holland (1994) estimates that during this transition time, the pO₂ level in the atmosphere increased rapidly from 1% to $\geq 15\%$ PAL.

Following formation of the uranium deposits and the fission reactors, the diagenesis of the

Franceville series continued until the FA sandstones reached a depth of 4000 m (Gauthier-Lafaye et al., 1989; Mathieu, 1999). At that level the temperature was 180–200 °C. This allowed a major silicification of the FA sandstones, which reduced the porosity of the rocks and protected the uranium deposits and the reactors from alteration.

9. Conditions for fission reactions

The conditions for the occurrence of nuclear fission reactions in a geological system have been discussed by Naudet (1991). Fission reactions occur spontaneously in ²³⁸U resulting in the production of fast neutrons. If these neutrons are slowed down, they may induce fission in ²³⁵U or ²³⁹Pu. Nuclear reactions can then be sustained. This can happen in a geological system if three conditions are met:

(1) The uranium ore must have a high uranium content. This increases the probability of spontaneous fission of ²³⁸U in the ore which initiates the fission reaction process and increases the probability of inducing fission in ²³⁵U which sustains the fission reaction.

(2) The fast neutrons produced by the spontaneous fission of ²³⁸U must be slowed down by migration through water or graphite. Naudet (1991) has shown that water should have been the main moderator for neutrons in the Oklo reactors, as it must have been present in the pore space of the sandstones and in clays that were important mineralogical phases in the reactors. Naudet (1991) also suggested that carbon may have played an important role in some organic matter rich reactors.

(3) The ²³⁵U content of the uranium should be high, so that the probability of a neutron hitting a fissile ²³⁵U atom and thus sustaining the nuclear reaction is also high. This last condition is satisfied in commercial nuclear plants by increasing the ²³⁵U/²³⁸U ratio of the nuclear fuel. At Oklo this condition was met because the radioactive decay constant for ²³⁵U (99.8485×10^{-10}) is smaller than that for ²³⁸U (1.55125×10^{-10}). Fig. 8 shows the variation of the ²³⁵U/²³⁸U ratio versus time. 2.0 Ga ago the ratio was similar to that of fuel in

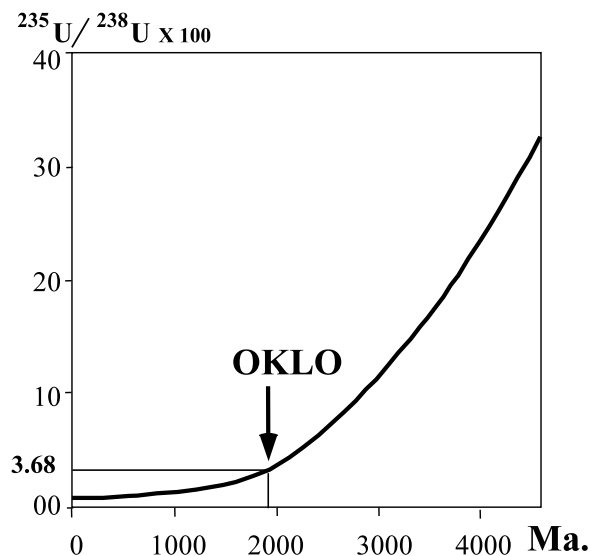


Fig. 8. Evolution of the $^{235}\text{U}/^{238}\text{U}$ ratio versus time. Age of the Oklo reactors is indicated.

pressured water reactor nuclear plants. There is little chance of finding natural fission reactors younger than 1.9 Ma because the amount of fissile ^{235}U was by then too small to sustain fission reactions in a natural environment. At ages > 2.0 Ga, the $^{235}\text{U}/^{238}\text{U}$ was sufficient to sustain fission in natural reactors and even very high at ages > 2.5 Ga. This is the main argument for predicting that fission reactors should have been common prior to 2.0 by. However, no traces of nuclear fission reactors have been found in pre-2.0 Ga uranium deposits such as those in the Witwatersrand or at Elliot Lake. This means that other conditions must be important as well. Clearly, a high concentration of uranium is of particular importance and this may be achieved only in certain geochemical conditions.

Fulfilment of conditions 1 and 3 allows a uranium deposit to reach the critical mass required to sustain a fission reaction. If the various physical (porosity) and chemical (content of various minerals and neutron poisons such as REE, B, and V) properties of the Oklo sandstones are taken into account, Naudet (1991) has shown that a sustained fission reaction would have occurred at Oklo

where the uranium content was 10% throughout one cubic meter of rock. In actual fact, the uranium content in the reactors was up to 60%. Such high concentrations in a sedimentary rock indicate that the uranium had been enriched during one or more diagenetic dissolution–precipitation episodes and implies that enough oxygen had been available in water to allow oxidation–reduction reactions of U to occur.

10. Preservation of the reactors

The preservation of the reactors over the long period of time is due to two main conditions: the stability of the West African craton and the protection of the reactors against aggressive agents.

The Francevillian series rests on Archean basement which is composed dominantly of the granitic Chaillu and North Gabon blocks that were emplaced between 3.9 and 3.2 Ga (Caen-Vachette et al., 1988; Ledru et al., 1989). The Archean rocks and the Francevillian series were subjected to an important tectonic disturbance that affected mainly the Western part of the craton, the so-called area of the Ogooué system (Gauthier-Lafaye, 1986; Ledru et al., 1989; Feybesse et al., 1998). This major tectonic phase was related to the 2.0 Ga Eburnean Orogeny which is also known in the Congo and Guyana cratons. In the Franceville basin, it is thought that this tectonic event took place during the first stage of the diagenesis of the sediments and therefore during the uranium mineralization event. The Franceville basin underwent only the distant consequences of this tectonic phase. It is likely that the major effect of this tectonic event was to help link the various aquifers leading to the formation of the uranium deposits. Since then, no major tectonic events have affected this craton during 2000 Ma (Gauthier-Lafaye, 1986; Ledru et al., 1989). During that 2000 Ma interval, only an extensional event, recorded by the intrusion of dolerite dykes that crosscut the Franceville series, occurred 970 Ma ago. It has been shown (Gauthier-Lafaye et al., 2000) that this event did not significantly affect the stability of the reactors.

Only minor redistributions of some elements (mainly Pb and U to some extent) occurred during that phase.

The main aggressive agent that could have destroyed the reactors is oxidised water. The clay gangue that embeds the reactor cores forms the first barrier in the form of an impermeable shield (Gerard, 1997). The large amount of organic matter associated with the reactors also forms a good protection against alteration (Nagy et al., 1991, 1993), able to easily neutralise the low volume of oxidised waters migrating through the slightly permeable clays. Moreover, most of the reactors were protected from weathering because they were located at depths >100 m. Only the reactor of Bangombé, which is just 12 m underground, has been affected by modern weathering. It is unclear when the recent uplift of the basin started. Geomorphological studies on the Okouma Plateau and of the Ogooué river (Emane Mba, 1997) and geological investigations of the Cenozoic series of the Western Gabon (Guiraud et al., 1992) conclude that the major phase of uplift of the Franceville basin and erosion of the upper formation of the Franceville series began during the early Eocene. It is likely that the uplift was progressive and did not belong to a single geological event. The only 'modern' age record is a U–Th date of $76\,500 \pm 6800$ years for a secondary tobernite that is related to the weathering of the uranium mineralization of Bangombé (Bros et al., 2000).

11. Summary and conclusions

The occurrence of manganese and uranium deposits and of nuclear reactors in the Franceville basin is not fortuitous. It results from conditions that could be achieved only during the very specific period of time corresponding to the initial oxygenation of Earth's atmosphere. It is generally admitted that during early Archean, oxygen produced by photosynthetic organisms induced Fe^{2+} oxidation/precipitation in iron deposits (BIF's), avoiding O_2 to escape into atmosphere. At this time oxidation/precipitation of Mn^{2+} was inhibited by the presence of dissolved Fe^{2+} (Roy, 2000)

and therefore Mn accumulated in sea water. During late Archean and Paleoproterozoic, the balance of Fe, supplied by oceanic hot springs, and of O_2 photosynthetic production, was altered and Fe^{2+} concentration in sea water drastically decreased. Then, the oxygen was consumed by oxidation/precipitation of Mn^{2+} and concentration of O_2 in atmosphere started to increase when all Mn in sea water precipitated. Afterward $p\text{O}_2$ in atmosphere allowed the oxidation of uranium and its precipitation and concentration in high grade deposits by redox reactions.

Our data agree with the model suggesting that an increase of oxygen in the atmosphere happened between 2150 Ma, the time of deposition of the Francevillian black shales devoid of uranium, and 1950 Ma, which corresponds to the period when uranium was mobilised in its oxidised state in the FA Formation. Holland (1994) estimates that during this period, the $p\text{O}_2$ level in the atmosphere increased rapidly from <1 to $\geq 15\%$ present atmospheric level. Furthermore, our data obtained on the carbon isotopes of organic matter and carbonates, on the Mn deposits and its Mn-proterite and on the U-deposits and the reactors strongly support this transition from a reduced to an oxygenated atmosphere–hydrosphere.

Two thousand one hundred and fifty million years ago, the intracratonic Francevillian basin was divided into sub-basins having different characteristics. In the Franceville sub-basin, fluvial conglomerates, marine clastic sediments and black shales are well developed whereas in the Okondja sub-basin, basic volcanism was important and was a possible source for manganese. However, the bulk of dissolved Mn accumulated in sea water during the Archean is probably a more important source. This time corresponds to a period of very intense development of marine life as reflected by the thickness of very organic-rich black shales, leading to basinal anoxia. The very low $\delta^{13}\text{C}$ of organic matter preserved at the edges of the Franceville basin attests to a large scale involvement of methanotrophic pathways in the formation of kerogens which imply a high CH_4 content in the atmosphere relative to the oxygen content.

The stability of uranium-bearing minerals (mainly monazites and possibly uraninites) under

low P_{O_2} favours their concentration in fluvial and coastal placers, similar to those in the uranium deposits of Witwatersrand. Under anoxic conditions, Mn can migrate over large distances. The fluctuations in sea levels and the local palaeogeographic conditions allowed Mn from distal volcanics to reach the edges of the Franceville basin, in zones where the development of the photosynthetic organisms increased the concentration of oxygen in the water, causing the precipitation of manganese oxides. In these zones the return to more reducing conditions was due to rapid burial possibly triggered by transgression episodes. This promoted the dissolution of the Mn-oxides and the precipitation of Mn-carbonates to form the protore of the Mn ore deposits. The progressive closure of the Franceville basin, marked by the depletion of $^{13}C_{org}$ enhanced the contrasts between the oxygenated edges of the basin and the anoxic zones corresponding to the more central parts of the basin. Thus, development of photosynthetic organisms, volcanic activity and basin morphology were important parameters controlling the formation of the Mn deposits.

The mobilisation of uranium in the Franceville basin occurred during diagenesis 1950 Ma ago, as the burial of the FA and FB formations reached 3000–4000 m. The migration of uranium is related to oxidation of the whole FA reservoir, alteration of the detrital uranium-bearing minerals and precipitation of iron oxides. This requires a complete recharge of the waters circulating in the FA reservoir and, therefore, water oxygenation in contact with the atmosphere. We believe that this event marks a significant increase in atmospheric oxygen. The oxidised uranium precipitated when it came into contact with hydrocarbons concentrated in tectonic traps. The occurrence of oxidation–reduction reactions allowed for the first time the formation of very high grade uranium ore deposits, which led in turn to nuclear fission reactions. If these oxidation–reduction reactions, related to the presence of oxygen in atmosphere, had occurred subsequently, nuclear fission reactions would not have occurred, because the abundances in fissile uranium 235 were too low after 1950 Ma. Thus, the natural nuclear reactors in the Franceville basin record a unique interval in Earth's history,

of high ^{235}U and transitional redox conditions, which explains the apparent absence of such remarkable phenomena in older or younger uranium deposits.

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