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Research article

The first application of Re–Os dating on Paleoproterozoic Francevillian sediments (Gabon)

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Abstract. Understanding the age of geological formations is essential to reconstruct Earth's history. Nevertheless, dating Proterozoic formations is a real challenge because they are often impacted by tectonic, magmatic or metamorphic phenomena. The sedimentary sequences of the Francevillian Basin are well preserved and have been dated previously using many methods (U–Pb, Ar–Ar, Rb–Sr, ...). Here, we applied the Re–Os dating method for the first time, specifically on the "FB" and "FD" formations containing a high organic matter (OM) content (up to10%). The age obtained, 2103 ± 11 Ma, is coherent with the previous studies. This data confirms the unusual quality of OM preservation and the chronology of the emergence of multicellular life occurring during the Lomagundi event.

Keywords. Dating, Re–Os, Francevillian, Paleoproterozoic, Gabon.

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1. Introduction

Dating geological formations is a major challenge in the study of ancient basins, in particular those of Precambrian age. In fact, these basins are generally impacted by tectonic [Caswell et al., 2021, D'Agrella-Filho et al., 2016], magmatic [Kabengele et al., 1991] metamorphic [Chatir et al., 2022, Prochaska et al., 1992], or diagenetic phenomena, that may severely alter isotopic signatures. Nevertheless, in some cases, these effects are minor [Gabbott et al., 2004, Ossa Ossa et al., 2013], allowing the history of the basin since its formation to be traced.

In Gabon, the Francevillian Basin is well known for the quality of preservation of its sedimentary formations. These host both uranium deposits [Bankole et al., 2016, Gauthier-Lafaye, 1986], which include the only known case of a natural nuclear reactor ever found in the world [Naudet, 1991, Neuilly et al., 1972], and the huge manganese deposits of Moanda [Pambo, 2004, Weber, 1997]. These sediments are also renowned as the rocks hosting the oldest multicellular life forms ever observed, which are present in an exceptional state of conservation [El Albani et al., 2010, 2014, 2023, Ikouanga et al., 2023].

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A variety of approaches have been used to date the various formations of the Francevillian Basin (Figure 1). The FA Formation was dated using U–Pb analyses of uraninite and Ar–Ar analyses of illite, giving ages of 2050 ± 30 Ma [Gancarz, 1978], and 2040 Ma–2010 Ma [Ossa Ossa et al., 2014], respectively. As the FB Formation includes the well-known manganese and uranium deposits, several dating attempts have been attempted. The Sm–Nd method was applied on clay fractions of the black shales, giving an age between 2099 ± 115 Ma and 2036 ± 79 Ma [Bros et al., 1992]. The age of the FB Formation was also constrained indirectly through Rb–Sr dating of intrusive syenites, yielding 2143 ± 143 Ma [Bonhomme et al., 1982]. In addition, U–Pb dating of zircons from these syenites provided ages varying between 2027 ± 55 Ma [Moussavou and Edou-Minko, 2006] and 2191 ± 13 Ma [Sawaki et al., 2017]. Horie et al. [2005] dated the FD Formation using the U–Pb method of zircons from cinerites, giving an age of 2083 ± 6 Ma. Similarly, U–Pb laser-MC-ICP-MS dating of zircons from this formation yielded an age of 2072 ± 29 Ma [Thiéblemont et al., 2009]. All of these dates show that the Francevillian Basin was formed around 2.1 Ma ago, a period that witnessed the maturation of organic matter associated with argilite sedimentation [Mossman et al., 2005].

In this new study, we present, for the first time, results from Re–Os dating of the Francevillian Formations, where the percentage of organic matter may exceed 10% (FB and FD Formations). Though the technique was applied to whole rock powders, the extracted Re and Os are hosted almost exclusively by organic material, especially when the digestion is done using a CrO_3–H_2SO_4 solution, as described below. The date obtained, 2103 ± 11 Ma, corresponds to the closing of the Re–Os system in organic matter at the time of the deposition of the Francevillian sediments. Thus, the age of these formations constitutes strong evidence of the emergence of multicellular life forms starting at 2103 ± 11 Ma.

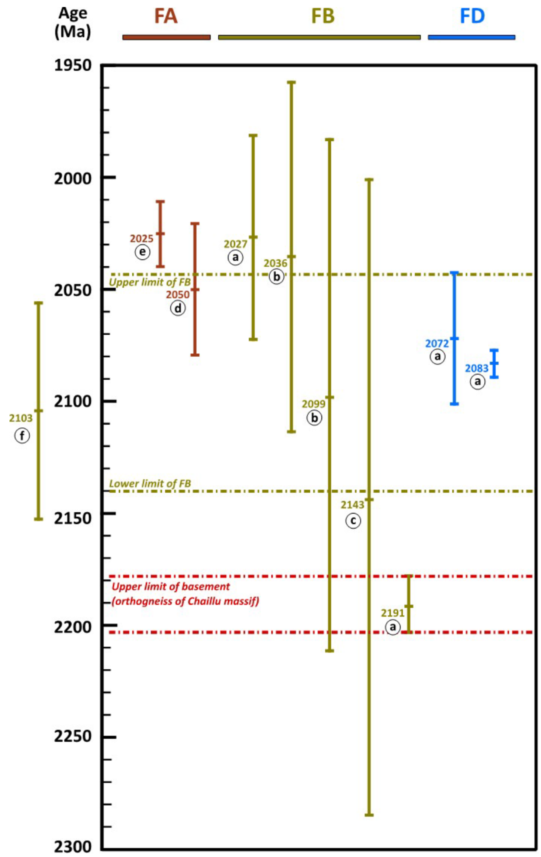

Figure 1. Comparison of different ages obtained on Francevillian formations, using 1/U–Pb (a), Sm–Nd (b) on clay fractions of black shales, Rb–Sr (c) on syenites 2/U–Pb (d) on uraninite, 3/Ar–Ar (e) on apatites and 4/ Re–Os (f) on organic matter.

2. Study area

The study area is located in southwestern Gabon, in the Francevillian Basin (Figure 2). This area is situated more than 80 km from the site of the Oklo natural nuclear reactor, so this unusual feature should have no effect on the studied radiometric systems. Four sedimentary formations of Paleoproterozoic age are described [Azziley Azzibrouck, 1986, Weber, 1968]. The FA Formation is formed of detrital and conglomeratic sediments. The uranium mineralization is found at the summit of this formation, at the boundary with the FB Formation [Bankole et al., 2016, Gauthier-Lafaye, 1986, Gauthier-Lafaye and Weber, 1989]. The FB Formation is subdivided into two sub-groups: FB1 and FB2 [Reynaud et al., 2018, Weber, 2016] with the manganese deposit found in between [Pambo, 2004, Weber, 1997]. The FB1 formation is composed of green marly sediments and turbiditic pelites, siltstones (FB1a), dolomitic and silty (FB1b) black shales, dolomites, and black shales very rich in organic matter. The FB2 formation is constituted of alternating pelites and sandstones (FB2a) and silty black shales (FB2b). It is the FB2b unit that hosts the oldest multicellular organisms [El Albani et al., 2010, 2014, 2019, Ikouanga et al., 2023]. The FC Formation is mainly formed of cherts and massive dolomites [Préat et al., 2011, Weber et al., 2016]. The FD Formation englobes mainly black shales of high organic matter content [Ngombi-Pemba et al., 2014, Thiéblemont et al., 2009] and constitutes the summit of the sedimentary pile of the Francevillian Basin.

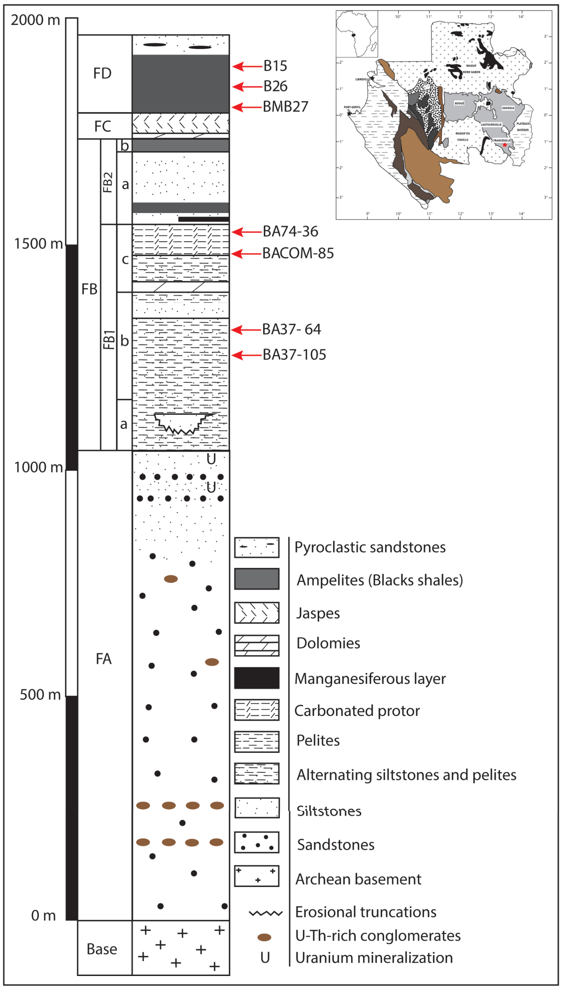

Figure 2. Lithostratigraphic log and geological map of the Francevillian Basin established from the sub-basin of Franceville, showing sampling zones [modified from El Albani et al., 2010].

3. Method

Re–Os dating was performed to obtain a depositional age of the black shales that host the Francevillian biota. A first series of six samples, taken from a vertical section from FB1b to FD, was analysed. About 0.2 g of powdered bulk sample was spiked with an appropriate quantity of a mixed ^{185}Re–^{190}Os isotopic tracer and digested in a solution of inverse aqua regia (2 ml HCl: 5 ml HNO_3) at 300 °C in a high-pressure Asher (Anton Paar HPA-S). Osmium was extracted from the resulting solution into Br_2 and purified by microdistillation, using techniques adapted from [Birck et al., 1997]. Rhenium was extracted from the remaining solution, after drying and redissolution in 0.8 N HNO_3, using chromatographic columns filled with anion exchange resin (AG1 X8). In order to reduce the scatter of the results, a series of four samples was replicated using a modified digestion technique recommended by Selby and Creaser [2003]. After spiking with the mixed isotopic tracer, samples were digested at 300 °C in 7 ml of a CrO_3 solution in 4 M H_2SO_4. The benefit of this latter method, relative to digestion in aqua regia, is that it is less likely to dissolve detrital phases, thus ensuring that the measured Re and Os are derived almost exclusively from organic matter. After sample digestion, Os was extracted into Br_2 and purified by microdistillation. Because of the presence of high contents of Cr^{6+}, separation of Re from the residual solution using anion exchange columns was not possible. Instead, Re was extracted by liquid–liquid exchange into iso-amylol, as recommended by Birck et al. [1997].

The purified Os fractions were analysed as OsO^{3-} ions by negative thermal ionization mass spectrometry (NTIMS) [Creaser et al., 1991, Völkening et al., 1991] using a Finnigan MAT262 instrument, at the CRPG laboratory (CNRS-University of Lorraine). Measurements were made by peak jumping in ion counting mode using an ETP electron multiplier. Data corrections for heavy oxides, mass fractionation and spike contribution were performed off-line, assuming the oxygen isotope composition of Nier ($^{18}O/^{16}O$ = 0.002045 and $^{17}O/^{16}O$ = 0.0003708) and a $^{192}Os/^{188}Os$ normalizing ratio of 3.08271. Over the analytical period, the value of the in-house Os standard was 0.17400 ± 0.00065 (82 analyses), consistent with the long-term value of this standard from the CRPG laboratory. Rhenium concentrations were determined by isotope dilution calculations after measurement of the isotope compositions by MC-ICP/MS (ThermoScientific Neptune). Mass fractionation was corrected by standard bracketing. Total Os blanks were 0.51 ± 0.24 (1s) pg during the analytical period. Total Re blanks were about 20 ± 16 (1s) pg for the samples digested in inverse aqua regia and 140 pg for the blank associated with the CrVI digestions, reflecting the commonly reported contamination of this reagent in Re. Nevertheless, as the same amount of Cr^{VI} solution was added to each sample, it was possible to correct for this contamination.

4. Results

The Re–Os data are presented in Table 1. For the three samples for which both techniques (aqua regia and CrO_3–H_2SO_4) were applied, the results are quite similar. Nevertheless, while the isotopic ratios of all of the samples are roughly aligned in a Re–Os isochron diagram (Figure 3a) the samples digested in the CrO_3–H_2SO_4 solution define a tighter correlation, in agreement with the findings of Selby and Creaser [2003]. As noted by these authors, digestion in CrO_3–H_2SO_4 solution accesses only hydrogeneous Os hosted by organic matter, while digestion in aqua regia may in addition liberate small amounts of Os from detrital phases, thus adding scatter to the isochron (Figure 3b). The well-defined correlation line obtained from the samples digested in CrO_3–H_2SO_4 solution, which includes four samples from the FB and FD Formations, indicates a Re–Os age of 2103 ± 11 Ma (MSWD = 2.6) with an initial $^{187}Os/^{188}Os$ ratio close to 0.108 ± 0.007 (all uncertainties 2s). We note that this age was obtained from only four samples and that the MSWD value is higher than the value of 1 expected for true isochrons. This means that the apparently tight limits on the age should be viewed with some caution. Nevertheless, the value obtained places a strong constrain on the age of the organic matter that hosts the Re and Os in these rocks. The isotope ratios $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ are higher in the black shales of the FB1b and FD Formations than in the FB1c Formation.

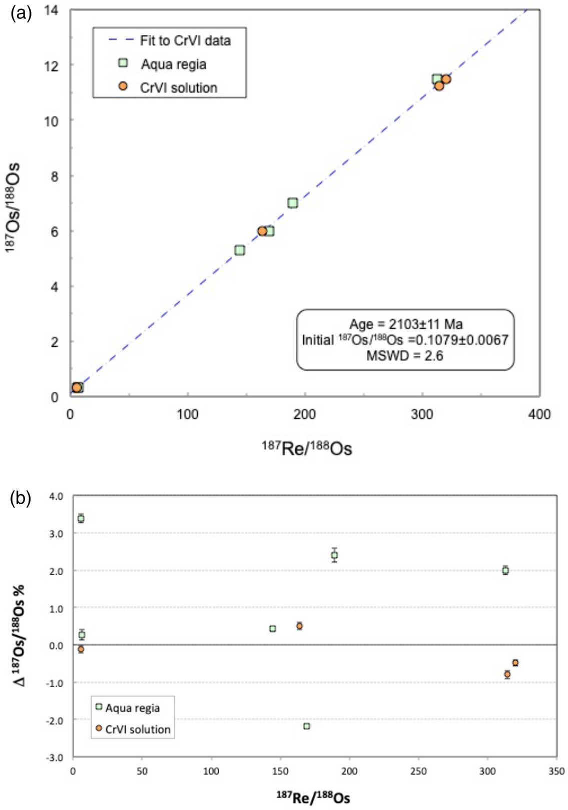

Figure 3. (a) Re–Os isochron obtained from organic matter from the FB-FD sequence of the Francevillian (Gabon) (b) Deviation in % of the measured $^{187}Os/^{188}Os$ ratio of each sample from the correlation line regressed through the samples dissolved in Cr^{VI} solution. It is clear that the samples dissolved in aqua regia display considerably more scatter, possibly indicating minor release of Os from detrital material in samples digested by this method.

5. Discussion

Very ancient sedimentary systems, such as the one in this study, are often well-adapted to dating by the Re–Os geochronometer [Hannah et al., 2008]. Transition metals, including Re and Os, are stabilized when associated with organic matter by forming organometallic complexes [Shock and Koretsky, 1995]. Rhenium and osmium are therefore concentrated in sedimentary organic matter, explaining their high concentrations in black shales [Ravizza and Turekian, 1989, Selby and Creaser, 2005]. It has

Table 1. Re–Os isotopic data obtained by digestion with Cr^{VI}–H_2SO_4 and aqua regia solutions

Sample name	CrVI: Samples digested in CrO_3 dissolved in 4N H_2SO_4				AR: Samples digested in inverse aqua regia					
	BA 37-64	BACOM-85	BMB27	B15	BA 37-105	BA 37-64	BACOM-85	BA 74-36	BB26	B15
Sample wreight (g)	0.23570	0.23391	0.16365	0.14748	0.20093	0.19992	0.19763	0.19883	0.20050	0.20242
$^{187}Os/^{188}Os$	11.471	0.3064	11.225	5.974	7.022	11.481	0.3191	0.343	5.274	5.9987
±2s	0.009	0.0003	0.012	0.006	0.013	0.013	0.0004	0.0005	0.003	0.0004
[Os] ppb	0.728	6.222	2.467	2.919	0.093	0.727	5.529	1.332	3.155	2.920
±2s (ppb)	0.002	0.165	0.008	0.007	0.002	0.003	0.094	0.004	0.007	0.009
[^{188}Os] (mole/g)	2.05×10^{-13}	4.24×10^{-12}	7.03×10^{-13}	1.16×10^{-12}	3.426×10^{-14}	2.05×10^{-13}	3.76×10^{-12}	9.04×10^{-13}	1.32×10^{-12}	1.15×10^{-12}
±2s (mole/g)	6.7×10^{-16}	1.1×10^{-13}	2.3×10^{-15}	2.6×10^{-15}	7.2×10^{-16}	9.2×10^{-16}	6.4×10^{-14}	2.1×10^{-15}	3.0×10^{-15}	3.6×10^{-15}
[Re] (ppb)	19.51	7.04	65.76	56.25	1.93	19.02	6.30	1.77	56.53	57.99
±2s (ppb)	0.25	0.14	0.64	0.37	0.16	0.16	0.16	0.16	0.16	0.16
^{187}Re (moles/g)	6.56×10^{-11}	2.37×10^{-11}	2.21×10^{-10}	1.89×10^{-10}	6.49×10^{-12}	6.39×10^{-11}	2.12×10^{-11}	5.94×10^{-12}	1.90×10^{-10}	1.95×10^{-10}
± 2s (mole/g)	8.4×10^{-13}	4.7×10^{-13}	2.2×10^{-12}	1.2×10^{-12}	5.38×10^{-13}	5.41×10^{-13}	5.47×10^{-13}	5.44×10^{-13}	5.41×10^{-13}	5.35×10^{-13}
$^{187}Re/^{188}Os$	320.2	5.58	314.3	163.7	189.3	312.7	5.6	6.6	144.3	169.0
±2s	4.2	0.18	3.2	1.1	16.2	3.0	0.17	0.60	0.52	0.70
TOC (%)	7.6	2.8	N.D	N.D	3.3	7.6	2.8	6.7	8.6	N.D

Listed uncertainties include blank variability as well as analytical uncertainties.

also been shown that the Re–Os system is usually not perturbed by organic matter maturation [Creaser et al., 2002]. Nevertheless, to guarantee a reliable result, the studied system must not have been disturbed by external influences such as hydrothermalism, metamorphism and many others. This is the case of the studied formations [El Albani et al., 2010, 2014, 2019, Ikouanga et al., 2023, Neuilly et al., 1972, Weber et al., 2016]. Finally, the use of a CrO^3–H_2SO_4 digestion medium greatly limits contamination with Re and Os derived from detrital material [Selby and Creaser, 2003], as shown by the better alignment of samples dissolved using this medium compared to those digested in aqua regia (Figure 3).

The FB Formation is composed primarily (around 80%) of marine shales, with organic matter contents varying between 0.5 and 10 wt% (total organic carbon or TOC) [Mossman et al., 2005]. The organic matter of the Francevillian sediments originated mainly from cyanobacteria remains [Mossman et al., 2005]. This material played an important role in the early stages of diagenesis [Mossman et al., 2005]. During burial, the organic matter is usually transformed into kerogen by polymerization [Stankiewicz et al., 2000]. During this process, the preservation of organic matter may be granted by clay-polymer interactions [Christidis, 2014]. The TOC contents cited above show that organic matter is not negligible in the Francevillian Formations and could provide material for dating.

The different dating techniques that have been used in the Francevillian Basin address the specific events to which they are sensitive: uranium mineralization [Gancarz, 1978], manganese mineralization [Bros et al., 1992], the setting up of the N'goutou volcanic complex [Moussavou and Edou-Minko, 2006, Sawaki et al., 2017], and localized hydrothermal processes [Ossa Ossa et al., 2014]. Nevertheless, some studies present ages that can be linked to sedimentary processes, mainly illitization during early diagenesis [Bros et al., 1992].

The various types of dating that have been done for the Francevillian Basin yield consistent ages (between 2.191 Ma and 2.036 Ma). In the FA Formation, dating was done by the Ar–Ar method on illites [Ossa Ossa et al., 2014] and by the U–Pb method on uraninite [Gancarz, 1978]. In the first case, the origin of the dated illites is not clearly defined, as they are formed during diagenetic or hydrothermal processes, and would postdate the depositional age. The obtained age corresponds to a lower limit, because the illites were formed during diagenesis or hydrothermalism. Concerning the second case, the uranium in the conglomeratic rocks is mobilized by oxidizing fluids [Gauthier-Lafaye and Weber, 1989]. Consequently, the uranium is brought in by oxidizing fluids and its age (2050 ± 30 Ma) defines a lower limit for the FA Formation.

Syenite intrusion affects solely at the base of the FB Formation, which is already in place [Moussavou and Edou-Minko, 2006, Sawaki et al., 2017]. The ages of these intrusions (respectively 2027 ± 55 Ma and 2143 ± 143) thus mark a lower time limit for the deposition. Bros et al. [1992] applied the Sm–Nd technique to date the clay fraction of black shales. To avoid possible detrital contribution, they separated clay fractions by centrifugation, then observed the phases using a transmission electron microscope, before proceeding to leaching of the black shales. However, the results of this dating are associated with the different illitization episodes during early diagenesis. The obtained ages (2099 ± 115 Ma and 2036 ± 79 Ma) do not correspond directly to the deposit of FB Formation sediments, but to their early diagenesis. The Rb–Sr dating of intrusive syenites (2143 ± 143 Ma) proposed by Bonhomme et al. [1982] represents only the limit between the FA and FB Formations without providing a precise time for the deposition of the FB Formation.

Zircons of tuffaceous sandstones of the FD Formation analysed by Laser-ICP/MS mark the most recent event [Thiéblemont et al., 2009]. Therefore, the depositional age is older than 2072 ± 29. Horie et al. [2005] also dated this formation (2083 ± 6 Ma). As the pyroclastic layer overlies the FD sediments, this well-defined age strongly constrains the minimal depositional age of these sediments.

Re–Os dating of Francevillian formations indicated an age of 2103 ± 11 Ma, corresponding to the age of closure of the Francevillian sedimentary system (from FB to FD). Thus, the fossilization age of the first multicellular life forms would have occurred during this period. The new Re–Os age for organic matter agrees with the age inferred from the $\delta^{13}C$ record of marine carbonates in the FB2 member [Canfield et al., 2013, El Albani et al., 2010], around 2.1 Ga ± 0.03. The high burial rate of organic matter associated with the deposition of the black shale was correlated with the Lomagundi Event, which represents the longest positive isotopic excursion of carbon in Earth history [Karhu and Holland, 1996, Prave et al., 2022]. Some authors link this event to the increase of oxygen in the atmosphere [Canfield et al., 2013, Karhu and Holland, 1996], whereas Melezhik et al. [1999] argue that it is due to paleo-environmental phenomena including organic burial. This event took place between 2110 Ma and 2060 Ma [Martin et al., 2004, Melezhik et al., 2013]. In consequence, the Re–Os age of organic matter of the Francevillian formations confirms the timing of the Lomagundi event.

6. Conclusion

A new depositional age of the Francevillian formations was obtained using the Re–Os dating method. The reliability of this age is supported by the relatively low MSWD value (2.6) determined for the isochron, which indicates that there has been only minimal perturbation of these samples in the intervening time. These Francevillian formations were deposited at 2103 ± 11 Ma, a period during which the Earth registered a high rate of carbon burial during the Lomagundi Event. The age obtained also confirms the date of the emergence of multicellular life forms that were identified in the FB2b Formation.

Declaration of interests

The authors do not work for, advise, own shares in, or receive funds from any organization that could benefit from this article, and have declared no affiliations other than their research organizations.

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References

Azziley Azzibrouck, G. (1986). *Sédimentologie et géochimie du Francevillien B (Proterozoique inferieur) métallogenie des gisements de manganese de Moanda, Gabon.* These de doctorat, Université de Strasbourg, Strasbourg 1. 224 p.

Bankole, O. M., El Albani, A., Meunier, A., Rouxel, O. J., Gauthier-Lafaye, F., and Bekker, A. (2016). Origin of red beds in the Paleoproterozoic Franceville Basin, Gabon, and implications for sandstone-hosted uranium mineralization. *Am. J. Sci.*, 316, 839–872.

Birck, J. L., Barman, M. R., and Capmas, F. (1997). Re–Os isotopic measurements at the femtomole level in natural samples. *Geostand. Newslett.*, 21(1), 19–27.

Bonhomme, M. G., Gauthier-Lafaye, F., and Weber, F. (1982). An example of lower proterozoic sediments: The Francevillian in Gabon. *Precambrian Res.*, 18, 87–102.

Bros, R., Stille, P., Gauthier-Lafaye, F., Weber, F., and Clauer, N. (1992). Sm–Nd isotopic dating of Proterozoic clay material: An example from the Francevillian sedimentary series, Gabon. *Earth Planet. Sci. Lett.*, 113, 207–218.

Canfield, D. E., Ngombi-Pemba, L., Hammarlund, E. U., Bengtson, S., Chaussidon, M., Gauthier-Lafaye, F., Meunier, A., Riboulleau, A., Rollion-Bard, C., Rouxel, O., Asael, D., Pierson-Wickmann, A.-C., and El Albani, A. (2013). Oxygen dynamics in the aftermath of the Great Oxidation of Earth's atmosphere. *Proc. Natl. Acad. Sci. USA*, 110, 16736–16741.

Caswell, B., Gilotti, J. A., Webb, L. E., McClelland, W. C., Kośmińska, K., Piepjohn, K., and von Gosen, W. (2021). $^{40}Ar/^{39}Ar$ dating of Paleoproterozoic shear zones in the Ellesmere–Devon crystalline terrane, Nunavut, Canadian Arctic. *Can. J. Earth Sci.*, 58, 1073–1084.

Chatir, A., Berger, J., Ennih, N., Triantafyllou, A., de Parseval, P., Errami, E., Diot, H., Baele, J.-M., Mohsine Aghzer, A., Monnier, C., and Boutaleb, M. (2022). Formation of the Nkob talc deposit by contact metamorphism and fluid infiltration into siliceous dolostones (Moroccan Anti-Atlas). *Ore Geol. Rev.*, 140, article no. 104629.

Christidis, G. (2014). B.K.G. Theng (2012) Formation and Properties of Clay-Polymer Complexes, 2nd edition. Developments in Clay Science, 4, Elsevier, Amsterdam, 511 pp, ISBN 978-0-444-53354-8. *Clay Miner.*, 49, 123–124.

Creaser, R. A., Papanastassiou, D. A., and Wasserburg, G. J. (1991). Negative thermal ion mass spectrometry of osmium, rhenium and iridium. *Geochim. Cosmochim. Acta*, 55, 397–401.

Creaser, R. A., Sannigrahi, P., Chacko, T., and Selby, D. (2002). Further evaluation of the Re–Os geochronometer in organic-rich sedimentary rocks: a test of hydrocarbon maturation effects in the Exshaw Formation, Western Canada Sedimentary Basin. *Geochim. Cosmochim. Acta*, 66, 3441–3452.

D'Agrella-Filho, M. S., Bispo-Santos, F., Trindade, R. I. F., and Antonio, P. Y. J. (2016). Paleomagnetism of the Amazonian Craton and its role in paleocontinents. *Braz. J. Geol.*, 46, 275–299.

El Albani, A., Bengtson, S., Canfield, D. E., Bekker, A., Macchiarelli, R., Mazurier, A., Hammarlund, E. U., Boulvais, P., Dupuy, J.-J., Fontaine, C., Fürsich, F. T., Gauthier-Lafaye, F., Janvier, P., Javaux, E., Ossa, F. O., Pierson-Wickmann, A.-C., Riboulleau, A., Sardini, P., Vachard, D., Whitehouse, M., and Meunier, A. (2010). Large colonial organisms with coordinated growth in oxygenated environments 2.1 Gyr ago. *Nature*, 466, 100–104.

El Albani, A., Bengtson, S., Canfield, D. E., Riboulleau, A., Rollion Bard, C., Macchiarelli, R., Ngombi Pemba, L., Hammarlund, E., Meunier, A., Moubiya Mouele, I., Benzerara, K., Bernard, S., Boulvais, P., Chaussidon, M., Cesari, C., Fontaine, C., Chi-Fru, E., Garcia Ruiz, J. M., Gauthier-Lafaye, F., Mazurier, A., Pierson-Wickmann, A. C., Rouxel, O., Trentesaux, A., Vecoli, M., Versteegh, G. J. M., White, L., Whitehouse, M., and Bekker, A. (2014). The 2.1 Ga old Francevillian biota: biogenicity, taphonomy and biodiversity. *PLoS One*, 9, article no. e99438.

El Albani, A., Konhauser, K., Somogyi, A., Ngwal'ghoubou Ikouanga, J., Lamboux, A., Blichert-Toft, J., Chi Fru, E., Fontaine, C., Mazurier, A., Riboulleau, A., Pierson-Wickmann, A.-C., and Albarède, F. (2023). A search for life in Palaeoproterozoic marine sediments using Zn isotopes and geochemistry. *Earth Planet. Sci. Lett.*, 612, article no. 118169.

El Albani, A., Mangano, M. G., Buatois, L. A., Bengtson, S., Riboulleau, A., Bekker, A., Konhauser, K., Lyons, T., Rollion-Bard, C., Bankole, O., Lekele Baghekema, S. G., Meunier, A., Trentesaux, A., Mazurier, A., Aubineau, J., Laforest, C., Fontaine, C., Recourt, P., Chi Fru, E., Macchiarelli, R., Reynaud, J. Y., Gauthier-Lafaye, F., and Canfield, D. E. (2019). Organism motility in an oxygenated shallow-marine environment 2.1 billion years ago. *Proc. Natl. Acad. Sci. USA*, 116, 3431–3436.

Gabbott, S. E., Xian-guang, H., Norry, M. J., and Siveter, D. J. (2004). Preservation of early Cambrian animals of the Chengjiang biota. *Geology*, 32, 901–904.

Gancarz, A. J. (1978). U–Pb age (205 × 109 years) of the Oklo uranium deposit. IAEA, International Atomic Energy Agency (Austria). *Panel Proc. Ser.*, 10(1), 513–520.

Gauthier-Lafaye, F. (1986). *Les gisements d'uranium du Gabon et les réacteurs d'Oklo. Modèle métallogénique de gîtes à fortes teneurs du Protérozoïque inférieur.* Sciences Géologiques, Bulletins et Mémoires, 78. Institut de Géologie – Université Louis-Pasteur, Strasbourg.

Gauthier-Lafaye, F. and Weber, F. (1989). The Francevillian (Lower Proterozoic) uranium ore deposits of Gabon. *Econ. Geol.*, 84, 2267–2285.

Hannah, J., Stein, H., Zimmerman, A., Yang, G., Melezhik, V., Filippov, M., Turgeon, S., and Creaser, R. (2008). Re–Os geochronology of shungite: A 2.05 Ga fossil oil field in Karelia. *Geochim. Cosmochim. Acta*, 72(12 (Suppl. 1)), article no. A351.

Horie, K., Hidaka, H., and Gauthier-Lafaye, F. (2005). U–Pb geochronolog and geochemistry of zircon from the Franceville series at Bidoudouma, Gabon. In *15th Annual Goldschmidt Conference, Moscow, United States.*

Ikouanga, J. N., Fontaine, C., Bourdelle, F., Abd Elmola, A., Aubineau, J., Bankole, O. M., Reisberg, L., Pierson-Wickmann, A.-C., Riboulleau, A., Trentesaux, A., Laforest, C., Meunier, A., and El Albani, A. (2023). Taphonomy of early life (2.1 Ga) in the francevillian basin (Gabon): Role of organic mineral interactions. *Precambrian Res.*, 395, article no. 107155.

Kabengele, M., Lubala, R. T., and Cabanis, B. (1991). Caractérisation pétrologique et géochimique du magmatisme ubendien du secteur de Pepa-Lubumba, sur le plateau des Marungu (Nord-Est du Shaba, Zaire). Signification géodynamique dans l'évolution de la chaîne ubendienne. *J. Afr. Earth Sci. (and the Middle East)*, 13, 243–265.

Karhu, J. and Holland, H. (1996). Carbon isotopes and the rise of atmospheric oxygen. *Geology*, 24(10), 867–870.

Martin, D., Briggs, D., and Parkes, R. (2004). Experimental attachment of sediment particles to invertebrate eggs and the preservation of soft-bodied fossils. *J. Geol. Soc.*, 161, 735–738.

Melezhik, V. A., Fallick, A. E., Martin, A. P., Condon, D. J., Kump, L. R., Brasier, A. T., and Salminen, P. E. (2013). 7.3 The Palaeoproterozoic perturbation of the global carbon cycle: The Lomagundi-Jatuli isotopic event. In Melezhik, V. A., Prave, A. R., Hanski, E. J., Fallick, A. E., Lepland, A., Kump, L. R., and Strauss, H., editors, *Reading the Archive of Earth's Oxygenation: Volume 3: Global Events and the Fennoscandian Arctic Russia - Drilling Early Earth Project, Frontiers in Earth Sciences*, pages 1111–1150. Springer, Berlin, Heidelberg.

Melezhik, V. A., Fallick, A. E., Medvedev, P. V., and Makarikhin, V. V. (1999). Extreme 13Ccarb enrichment in ca. 2.0 Ga magnesite–stromatolite–dolomite–'red beds' association in a global context: a case for the world-wide signal enhanced by a local environment. *Earth Sci. Rev.*, 48, 71–120.

Mossman, D., Gauthier-lafaye, F., and Jackson, S. (2005). Black shales, organic matter, ore genesis and hydrocarbon generation in the Paleoproterozoic Franceville Series, Gabon. *Precambrian Res.*, 137, 253–272.

Moussavou, M. and Edou-Minko, A. (2006). Contribution à l'histoire thermo-tectonique précambrienne du complexe annulaire de Ngoutou par la géochimie et la géochronologie U/Pb sur minéraux accessoires (Bassin Francevillien d'Okondja, Gabon). *Afr. Geosci. Rev.*, 13, 53–61.

Naudet, R. (1991). *OKLO: Fossil Nuclear Reactors. Physical Study. OKLO: des reacteurs nucleaires fossiles. Etude physique.* Série synthèses. Eyrolles.

Neuilly, M., Bussac, J., Frejacques, C., Nief, G., Vendryes, G., and Yvon, J. (1972). Sur l'existence dans un passé reculé d'une réaction en chaîne naturelle de fissions, dans le gisement d'uranium d'Oklo (Gabon). *C. R. Acad. Sci. Ser.*, 275, 1847–1849.

Ngombi-Pemba, L., Albani, A. E., Meunier, A., Grauby, O., and Gauthier-Lafaye, F. (2014). From detrital heritage to diagenetic transformations, the message of clay minerals contained within shales of the Palaeoproterozoic Francevillian Basin (Gabon). *Precambrian Res.*, 255, 63–76.

Ossa Ossa, F., El Albani, A., Hofmann, A., Bekker, A., Gauthier-Lafaye, F., Pambo, F., Meunier, A., Fontaine, C., Boulvais, P., Pierson-Wickmann, A.-C., Cavalazzi, B., and Macchiarelli, R. (2013). Exceptional preservation of expandable clay minerals in the ca. 2.1Ga black shales of the Francevillian Basin, Gabon and its implication for atmospheric oxygen accumulation. *Chem. Geol.*, 362, 181–192.

Ossa Ossa, F., Hofmann, A., Vidal, O., Kramers, J. D., Agangi, A., Belyanin, G. A., and Mayaga-Mikolo, F. (2014). Hydrothermal clay mineral formation in the uraniferous Paleoproterozoic FA Formation, Francevillian Basin, Gabon. *Precambrian Res.*, 246, 134–149.

Pambo, F. (2004). *Conditions de formation des carbonates de manganèse protézoïques et analyse minéralogique et géochimique des minerais à bioxydes de manganèse associés dans le gisement de Moanda (Sud-Est, Gabon).* Thèse de doctorat, Université de Bourgogne, Dijon. 274 p.

Prave, A. R., Kirsimze, K., Lepland, A., Fallick, A. E., Kreitsmann, T., Deines, Yu. E., Romashkin, A. E., Rychanchik, D. V., Medvedev, P. V., Moussavou, M., Bakakas, K., and Hodgskiss, M. S. W. (2022). The grandest of them all: the Lomagundi–Jatuli Event and Earth's oxygenation. *J. Geol. Soc.*, 179(1), article no. jgs2021-036.

Préat, A., Bouton, P., Thiéblemont, D., Prian, J.-P., Ndounze, S. S., and Delpomdor, F. (2011). Paleoproterozoic high δ13C dolomites from the Lastoursville and Franceville basins (SE Gabon): Stratigraphic and synsedimentary subsidence implications. *Precambrian Res.*, 189, 212–228.

Prochaska, W., Mogessie, A., and Raith, J. G. (1992). Formation of the talc deposit of Kibanda (Rwanda) and its relation to the regional metamorphic evolution. *J. Afr. Earth Sci. (and the Middle East)*, 14, 499–509.

Ravizza, G. and Turekian, K. K. (1989). Application of the 187Re–187Os system to black shale geochronometry. *Geochim. Cosmochim. Acta*, 53, 3257–3262.

Reynaud, J.-Y., Trentesaux, A., El Albani, A., Aubineau, J., Ngombi-Pemba, L., Guiyeligou, G., Bouton, P., Gauthier-Lafaye, F., and Weber, F. (2018). Depositional setting of the 2·1 Ga Francevillian macrobiota (Gabon): Rapid mud settling in a shallow basin swept by high-density sand flows. *Sedimentology*, 65, 670–701.

Sawaki, Y., Moussavou, M., Sato, T., Suzuki, K., Ligna, C., Asanuma, H., Sakata, S., Obayashi, H., Hirata, T., and Edou-Minko, A. (2017). Chronological constraints on the Paleoproterozoic Francevillian Group in Gabon. *Geosci. Front.*, 8, 397–407.

Selby, D. and Creaser, R. (2003). Re–Os geochronology of organic rich sediments: An evaluation of organic matter analysis methods. *Chem. Geol.*, 200, 225–240.

Selby, D. and Creaser, R. (2005). Direct radiometric dating of hydrocarbon deposits using rhenium–osmium isotopes. *Science*, 308, 1293–1295.

Shock, E. L. and Koretsky, C. M. (1995). Metal-organic complexes in geochemical processes: Estimation of standard partial molal thermodynamic properties of aqueous complexes between metal cations and monovalent organic acid ligands at high-pressures and temperatures. *Geochim. Cosmochim. Acta*, 59, 1497–1532.

Stankiewicz, B. A., Briggs, D. E. G., Michels, R., Collinson, M. E., Flannery, M. B., and Evershed, R. P. (2000). Alternative origin of aliphatic polymer in kerogen. *Geology*, 28, 559–562.

Thiéblemont, D., Castaing, C., Billa, M., Bouton, P., and Préat, A. (2009). *Notice explicative de la carte géologique et des ressources minérales de la République gabonaise à 1/1 000 000.* DGMG Editions - Ministère des Mines, du Pétrole, des Hydrocarbures, Libreville.

Völkening, J., Walczyk, T., and Heumann, K. G. (1991). Osmium isotope ratio determinations by negative thermal ionization mass spectrometry. *Int. J. Mass Spectrom. Ion Processes*, 105, 147–159.

Weber, F. (1968). *Une série précambrienne du Gabon : le Francevillien. Sédimentologie, géochimie, relations avec les gîtes minéraux associés.* Thèse Université Louis Pasteur Strasbourg, Mémoire Service Cartes Géologique Alsace-Lorraine. 331 p.

Weber, F. (1997). Evolution of lateritic manganese deposits. In Paquet, H. and Clauer, N., editors, *Soils and Sediments: Mineralogy and Geochemistry*, pages 97–124. Springer, Berlin, Heidelberg.

Weber, F. (2016). The 2-Ga Eburnean Orogeny in Gabon and the opening of the Francevillian intracratonic basins: A review 15. *C. R. Geosci.*, 348(8), 572–586.

Weber, F., Gauthier-Lafaye, F., Whitechurch, H., Ulrich, M., and El Albani, A. (2016). The 2-Ga Eburnean Orogeny in Gabon and the opening of the Francevillian intracratonic basins: A review. *C. R. Geosci.*, 348, 572–586.