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**The first application of Re–Os dating on Paleoproterozoic Francevillian sediments
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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 to 10%). 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 argillite 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 $\text{CrO}_3\text{--H}_2\text{SO}_4$ 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.

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

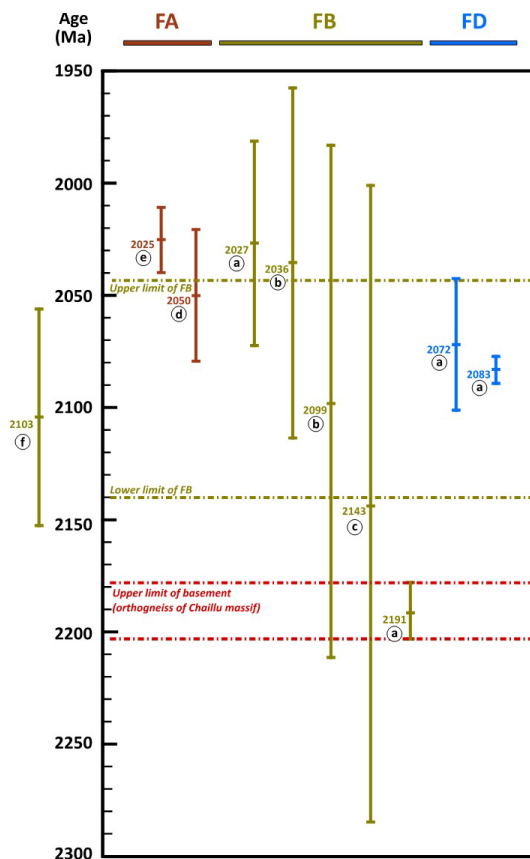


Figure 1. Comparison of different ages obtained on Francevillian formations, using 1/U–Pb (a), Sm–Nd (b) on clay fractions of black shales, Rb–Sr (c) on syenites 2/U–Pb (d) on uraninite, 3/Ar–Ar (e) on apatites and 4/ Re–Os (f) on organic matter.

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.

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

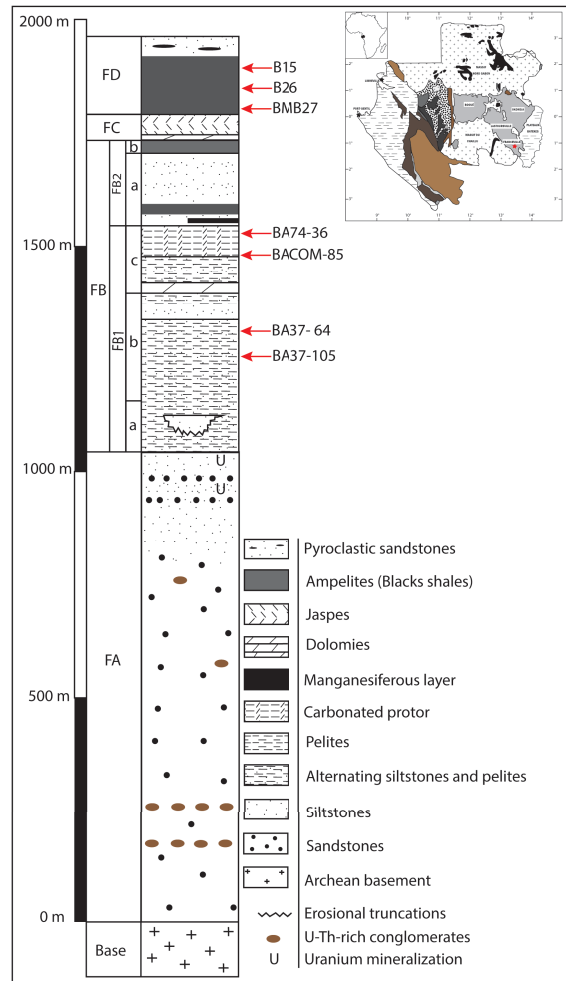


Figure 2. Lithostratigraphic log and geological map of the Francevillian Basin established from the sub-basin of Franceville, showing sampling zones [modified from El Albani *et al.*, 2010].

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 ($^{18}\text{O}/^{16}\text{O} = 0.002045$ and $^{17}\text{O}/^{16}\text{O} = 0.0003708$) and a $^{192}\text{Os}/^{188}\text{Os}$ 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 CrO₃–H₂SO₄) 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 CrO₃–H₂SO₄ solution define a tighter correlation, in agreement with the findings of Selby and Creaser [2003]. As noted by these authors, digestion in CrO₃–H₂SO₄ solution accesses only homogeneous 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 CrO₃–H₂SO₄ 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 $^{187}\text{Os}/^{188}\text{Os}$ 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 $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ are higher in the black shales of the FB1b and FD Formations than in the FB1c Formation.

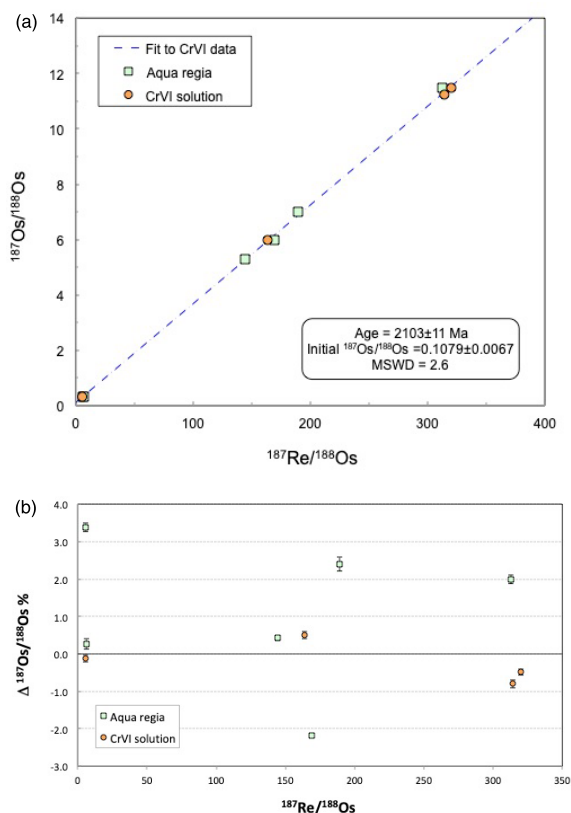


Figure 3. (a) Re–Os isochron obtained from organic matter from the FB-FD sequence of the Francevillian (Gabon) (b) Deviation in % of the measured $^{187}\text{Os}/^{188}\text{Os}$ ratio of each sample from the correlation line regressed through the samples dissolved in Cr^{VI} solution. It is clear that 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}–H₂SO₄ and aqua regia solutions

Sample name	CrVI: Samples digested in CrO ₃ dissolved in 4N H ₂ SO ₄					AR: Samples digested in inverse aqua regia					
	BA 37-64	BACOM-85	BMB27	B15	B15	BA 37-105	BA 37-64	BACOM-85	BA 74-36	BE26	B15
Sample weight (g)	0.23570	0.23391	0.16365	0.14748	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	5.974	7.022	11.481	0.3191	0.343	5.274	5.9987
±2s	0.009	0.0003	0.012	0.006	0.006	0.013	0.013	0.0004	0.0005	0.003	0.0004
[Os] ppb	0.728	6.222	2.467	2.919	2.919	0.093	0.727	5.529	1.332	3.155	2.920
±2s (ppb)	0.002	0.165	0.008	0.007	0.007	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}	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}	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	56.25	1.93	19.02	6.30	1.77	56.53	57.99
±2s (ppb)	0.25	0.14	0.64	0.37	0.37	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}	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}	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	163.7	189.3	312.7	5.6	6.6	144.3	169.0
±2s	4.2	0.18	3.2	1.1	1.1	16.2	3.0	0.17	0.60	0.52	0.70
TOC (%)	7.6	2.8	N.D	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 $\text{CrO}_3\text{--H}_2\text{SO}_4$ 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) [Mossmann *et al.*, 2005]. The organic matter of the Francevillian sediments originated mainly from cyanobacteria remains [Mossmann *et al.*, 2005]. This material played an important role in the early stages of diagenesis [Mossmann *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 $\delta^{13}\text{C}$ record of marine carbonates in the FB2 member [Canfield *et al.*, 2013, El Albani *et al.*, 2010], around $2.1 \text{ Ga} \pm 0.03$. 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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