



Petrology, geochemistry

No proof from carbon isotopes in the Francevillian (Gabon) and Onega (Fennoscandian shield) basins of a global oxidation event at 1980–2090 Ma following the Great Oxidation Event (GOE)

Sur l'absence de preuve d'une oxydation globale, faisant suite au Grand Évènement oxydant (GOE) à 1980–2090 Ma, basée sur les isotopes du carbone dans les bassins de Franceville (Gabon) et d'Onéga (Bouclier fennoscandinave)

Francis Weber*, François Gauthier-Lafaye

LHYGES, université de Strasbourg, CNRS, 1, rue Blessig, 67084 Strasbourg cedex, France

ARTICLE INFO

Article history:

Received 5 July 2012

Accepted after revision 11 December 2012

Available online 16 January 2013

Presented by Georges Pédor

Keywords:

Proterozoic

Lomagundi event

Carbon isotopes

Great oxidation event

Francevillian

Organic matter

Mots clés :

Protérozoïque

Épisode Lomagundi

Isotopes du carbone

Grand événement oxydant

Francevillien

Matière organique

ABSTRACT

Highly depleted C isotope composition of organic matters from the Onega (Fennoscandian shield) and Francevillian (Gabon) basins are differently interpreted. Kump et al. (2011) suggested the occurrence of a massive and global oxidation event during the period of 1980–2090 Ma, which follows the Great Oxidation Event (2450–2320 Ma) (Bekker et al., 2004). Inversely, Gauthier-Lafaye and Weber (2003) invoke the possible action of methanotrophic microorganisms to explain the $\delta^{13}\text{C}$ values as low as -46% measured in the Franceville basin. Here we present the isotope data available in the Franceville basin in order to discuss these two interpretations. The lack of any $\delta^{13}\text{C}$ correlation between organic matter and carbonate in the Franceville basin does not allow the consideration of a massive and global oxidation event.

© 2013 Published by Elsevier Masson SAS on behalf of Académie des sciences.

R É S U M É

Les mesures de la composition isotopique du carbone des matières organiques des bassins d'Onéga (Bouclier fennoscandinave) et de Franceville (Gabon) ont révélé des valeurs très basses qui ont été différemment interprétées. Kump et al. (2011) suggèrent l'existence d'une oxydation globale et massive pendant la période 1980 à 2090 Ma, qui suit le Grand Évènement oxydant (GOE) (2450–2320 Ma) (Bekker et al., 2004). Inversement, Gauthier-Lafaye et Weber (2003) invoquent l'action possible de microorganismes méthanotrophes pour expliquer des valeurs de $\delta^{13}\text{C}$ aussi basses que -46% , mesurées dans le bassin de Franceville. Nous présentons ici les mesures isotopiques effectuées dans le bassin de Franceville pour discuter ces deux hypothèses. L'absence de corrélation entre les valeurs de $\delta^{13}\text{C}$ des matières organiques et des carbonates ne permet pas d'envisager une période d'oxydation massive et globale dans le bassin de Franceville.

© 2013 Publié par Elsevier Masson SAS pour l'Académie des sciences.

* Corresponding author.

E-mail addresses: weber.francis@neuf.fr (F. Weber), fgl@unistra.fr (F. Gauthier-Lafaye).

1. Introduction

Two Paleoproterozoic basins, namely the Onega basin (Russia) and the Francevillian basin (Gabon) show very negative $\delta^{13}\text{C}$ values of organic matters (up to more than -40‰ PDB). The origin of this important negative excursion remains unclear. Two very different interpretations are proposed. Kump et al. (2011) suggest that this anomaly is due to massive oxidation of organic matter reflecting the establishment of an oxygen-rich atmosphere in the aftermath of the Great Oxidation Event (GOE) (2450–2320 Ma) (Bekker et al., 2004). Gauthier-Lafaye and Weber (2003) meanwhile suggest that in the basin of Franceville this anomaly, not being related to a similar negative $\delta^{13}\text{C}$ anomaly in carbonate, should result from another process. It is suggested that the increase of CH_4 in ocean and atmosphere due to important development of methanogenic organisms played an important role. Here we present all available data to best discuss these interpretations.

2. Brief presentation of the Francevillian series

The Francevillian basins are located in the southeastern part of the Republic of Gabon. It covers an area of 35,000

km^2 and it is bounded by crystalline terrain of Archean age (Weber, 1968; Feybesse et al., 1998). The series have been deposited in intracratonic basins about 2100 Ma ago (Hories et al., 2005). Sediments are non-metamorphosed and essentially of epicontinental detrital and volcanic origin. The southeastern part of the Francevillian area is named Franceville basin (Fig. 1). In this basin, the lithostratigraphic succession defined by Weber (1968) consists of five major formations which are from the bottom to the top FA, FB, FC, FD and FE:

The FA formation (up to 1000 m thick) is made of sandstones and conglomerates; fluviatile at the bottom, they become deltaic and of coastal bars at the top. Three facies occur in a sequence of red, green and black colored sediments (Gauthier-Lafaye and Weber, 1989). The contact between sediments of different colors is clearly discordant on the bedding, which indicates that coloration is not of sedimentary origin but was acquired during the diagenetic stage. Black sandstones are restricted to the higher levels of the formation. Their color is mainly due to organic matter in pore spaces; this organic matter consists of solidified petroleum (pyrobitumen) that fills the primary and secondary porosity of the sandstones and the fractures (Gauthier-Lafaye and Weber, 1989). The red color is due to

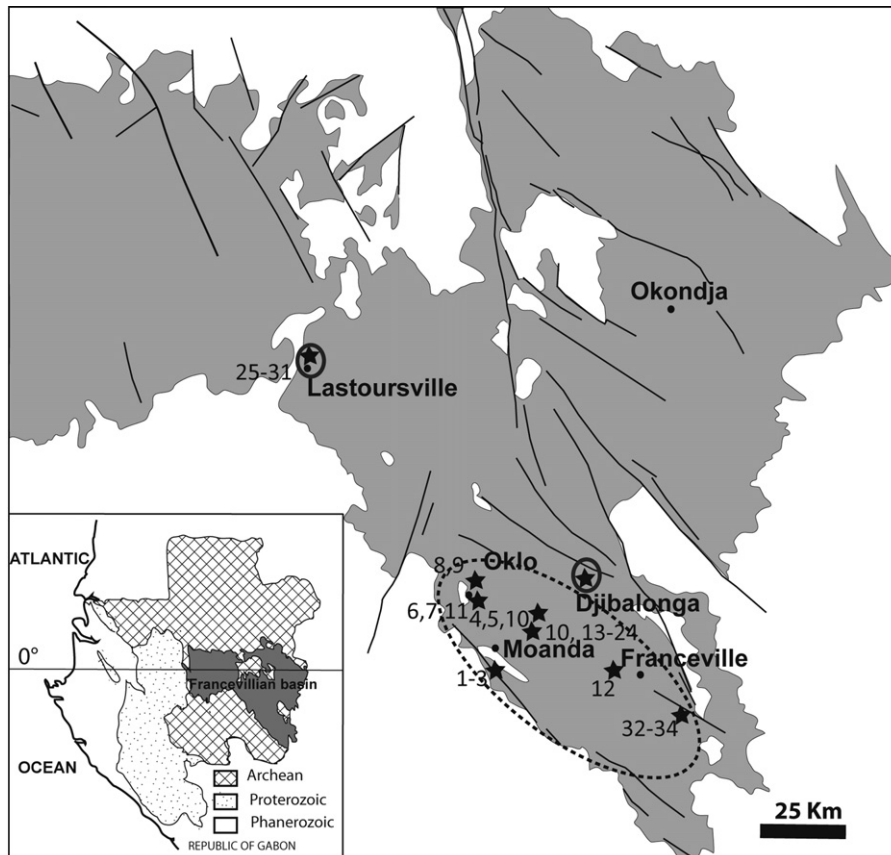


Fig. 1. Map of the Francevillian basin showing the location of the samples reported in Table 1. The ellipse in dashed line define the Franceville basin. Stars: location of the samples reported in Table 1. Circles: location of the samples analyzed by Pr at et al. (2011).

Fig. 1. Carte du Bassin francevillien montrant la localisation des  chantillons report s dans le Tableau 1. L'ellipse en pointill s d finit le bassin de Franceville.  toiles : position des  chantillons report s dans le Tableau 1. Cercles : position des  chantillons analys s par Pr at et al. (2011).

Table 1

$\delta^{13}\text{C}$ analytical data on organic matter and carbonates from the Franceville basin. Analyses were performed at the Max-Planck-Institut in Mainz and published by Weber et al. (1983), Gauthier-Lafaye (1986) and Gauthier-Lafaye and Weber (1989, 2003).

Tableau 1

Analyses du $\delta^{13}\text{C}$ des matières organiques et des carbonates du bassin de Franceville. Les analyses ont été effectuées au Max-Planck-Institut à Mayence et publiées par Weber et al. (1983), Gauthier-Lafaye (1986) et Gauthier-Lafaye et Weber (1989, 2003).

Number	Sample identification	Stratigraphic position	Petrography	% C total	% C org	$\delta^{13}\text{C}$ ‰ Carbonate	$\delta^{13}\text{C}$ ‰ OM
Center of the basin							
1	MAB 411 m ^b	FA inf.	Calcite veinlets	4.1	0.0	-2.8	-
2	MAB 237 m ^b	FA moy.	Sandstone with dolomitic cement	1.3	0.2	2.1	-
3	MAB 195 m ^b	FA moy.	Sandstone with dolomitic cement	1.1	0.0	2.4	-
4	BA2 83 m ^b	FA sup.	Sandstone with pyrobitumen	0.3	0.3	-	-22.9
5	BA2 71 m ^b	FA sup.	Sandstone with dolomitic cement	0.3	0.3	-	-24.9
6	Oklo open pit: GL 522 ^a	FA sup.	Pyrobitumen	43.0	43.0	-	-22.7
7	Oklo open pit: GL2372 ^a	FA sup.	Pyrobitumen	32.4	32.0	-	-21.8
8	S62A 32.6 m ^b	FB1 inf.	Sandstone with carbon cement	2.4	1.2	-1.8	-23.5
9	SH4 29.6 m ^b	FB1 inf.	Dolomitic turbidite	11.3	0.1	3.5	-25.8
10	BA-1 266.5 m ^c	FB1 inf.	Siderite in dolomite	7.5	0.8	-1.7	-33.1
11	OK21 185.5 m ^b	FB1 moy.	Black shale	8.1	6.8	-	-27.1
12	RFM 362 ^a	FB1 moy.	Coal of Mikouloungou	25.9	25.8	-	-31.7
13	SD 14-330 ^c	FB1 sup.	Siderite	8.1	0.6	-13.4	-29.9
14	SD 11-58 ^c	FB1 sup.	Mg-siderite	7.1	0.5	-11.1	-25.7
15	SD 14-322 ^c	FB1 sup.	Mn, Ca, Mg-carb.+OM	9.3	3.8	-4.1	-34.0
16	SD 13-259 ^c	FB1 sup.	Mn, Ca, Mg-carb.+OM	12.5	6.2	0.6	-34.7
17	SD 11-32 ^c	FB1 sup.	Mn, Ca, Mg-carb.+OM	11.0	2.8	-3.0	-36.4
18	SD 13-235 ^c	FB1 sup.	Mn-dolomite	5.3	0.5	-10.1	-34.3
19	SD 12-144 ^c	FB1 sup.	Siderite + pyrite + phosphate	3.1	1.7	0.7	-24.5
20	SD 12-135 ^c	FB1 sup.	Mn, Ca, Mg-carb.+OM	12.5	6.1	-2.6	-34.3
21	SD 12-124 ^c	FB1 sup.	Mn-dolomite + OM	7.7	3.9	-1.1	-36.8
22	SD 12-123 ^c	FB1 sup.	Mn-dolomite + OM	7.5	3.0	-7.2	-38.2
23	SD 12-109 ^c	Top of FB1	Black shale	5.0	4.8	-	-36.0
24	SD 12-105 ^c	Top of FB1	Black shale	5.8	5.4	-	-37.5
32	RFM-104B ^a	FC	Black shale + pyrite	9.9	9.9	-	-46.2
33	FW-53-110 ^a	FC	Black shale	17.1	17.1	-	-44.2
34	RFM 189 ^a	FD	Black shale	10.6	10.6	-	-40.4
Edge of the basin							
25	FW-66-457A ^a	FB-C	Pyrobitumen	82.0	82.0	-	-42.9
26	FW-66-457B ^a	FB-C	Calcite in void	11.6	0.3	-0.4	-42.2
27	FW-66-457AB ^a	FB-C	Pyrobitumen + calcite	15.4	8.3	-0.2	-45.4
28	FW-66-457 C ^a	FB-C	Dolomite	12.2	0.0	4.7	-
29	FW-66-440 ^a	FB-C	Dolomite	12.1	0.0	6.3	-37.7
30	FW-66-442 ^a	FB-C	Stinking-dolomite	12.7	1.8	2.6	-39.5
31	FW-66-443 ^a	FB-C	Black shale + pyrite	9.0	9.0	-	-36.9

^a Field samples: FW (Weber, 1968); GL (Gauthier-Lafaye, 1986); RFM (Favre-Mercuret, 1965).

^b Drill cores from Compagnie des mines d'uranium de Franceville (COMUF).

^c Drill cores from Compagnie minière de l'Ogooué (COMILOG).

hematite impregnation of the clay matrix; hematite also surrounds the quartz grains between their detrital boundaries and their overgrowths, suggesting that the main siliceous diagenesis occurred after an oxidation event. Uranium deposition took place at the top of the FA formation, during this oxidation event (Gauthier-Lafaye and Weber, 1989). In one of these deposits, the famous natural fission reactors of Oklo were discovered in 1972 (Gauthier-Lafaye et al., 1989; Neuilly et al., 1972).

The FB formation (300 to 1000 m. thick) is dominated by various shales including black shales with interbedded breccia and sandstones of turbiditic origin (Azzibrouck-Azzilez, 1986; Mossmann et al., 2005; Thiéblemont et al., 2009). The occurrence of large olistolithes made of dolomites and chert blocks interbedded in the basal black shales and turbiditic sediments at Oklo is a good example

of this type of sedimentation (Gauthier-Lafaye, 1986). Major manganese deposits are mined in lateritic formations developed on a Mn-rich unit of the upper part of the FB formation. The protore of the ore deposit consists of black shales containing Mn-rich carbonates (Weber, 1997). It lays over a small iron formation containing siderite, pyrite and greenalite. In the upper part of the FB formation, large colonial organisms were discovered (El Albani et al., 2010). They developed in a shallow water oxygenated environment. They are the oldest macro-fossils ever discovered in the world at the present time.

The FC formation (10 to 40 m thick) consists of stromatolitic cherts and evaporitic dolomites interbedded with minor black shales and corresponds to a quasi-emersion episode (Bertrand-Sarfati and Potin, 1994; Prétat et al., 2011). It should be emphasized that at the edge of the

Franceville basin and on shelves, stromatolythic cherts and evaporitic dolomites of “FC facies” appear immediately on FA sandstones and on Archean basement. They were deposited in shallow and restricted areas forming the edges of the basin during deposition of the FB black shales and turbidites, and later in a larger area when the FB basin was isolated. Consequently, during the FB episode, cherts and dolomites were deposited on the edge of the Franceville basin whereas black shales and turbidites deposited in more distal areas at the same time.

The FD formation starts with black shales similar to the one interlayered in the cherts of the FC formation. It is characterized by the occurrence of rhyolitic tuffs and epiclastic sandstones interlayered with shales. Volcano-clastic sediments of the FD formation represent a new extension event defining a large basin whose edges are unknown. The rhyolitic tuffs were precisely dated by U–Pb analyses on zircons: 2083 ± 6 Ma (Horie et al., 2005).

The FE formation consists of sandstones, probably resulting of the erosion of the Ogooué orogenic belt (Thiéblemont et al., 2009).

3. Isotopic analyses of C performed in the Francevillian Series

The first isotopic analyses of C and O were performed by M. Schidlowski at the Max-Planck-Institut in Mainz and presented at an European meeting (Weber et al., 1983). For each sample, carbon isotopes analyses of organic matter and carbonates have been performed. These analyses were partially published by Gauthier-Lafaye (1986) and Gauthier-Lafaye and Weber (1989, 2003). In Table 1, however, we present all the data that were available at this time. The location of the samples is shown in Fig. 1. We must here consider two sets of samples depending on their paleogeographic position at the edge of the Franceville basin or in its central part.

3.1. Analyses of samples from the center part of the Franceville basin.

Fig. 2 reports the $\delta^{13}\text{C}$ values for organic matter and carbonates of the samples located in the central part of the Franceville basin.

The $\delta^{13}\text{C}$ values of organic matter from the top of the FA formation (pyrobitumen) and from the black shales of the basal FB formation are quite similar, ranging between -20 and -30‰ (sample 4 to 11). This suggests that the petroleum diagenesis did not affect significantly the isotopic composition of the organic matter. The data on the $\delta^{13}\text{C}$ in the FB formation shows a trend toward negative values with -40‰ at the top of the formation. A similar trend has been observed by Cortial et al. (1990). It has to be noted that the lower $\delta^{13}\text{C}$ values (-40 to -46‰) are for samples representing the shallower environment of this sequence, i.e. from the FC formation and the basal FD black shales (Gauthier-Lafaye and Weber, 2003). In the central part of the basin, the trend of the $\delta^{13}\text{C}$ values of organic matter toward negative values must be correlated with the decrease of the bathymetry (Gauthier-Lafaye and Weber, 2003), the extreme values ($< -40\text{‰}$) being reached in the FC formation when the basin was almost emerged.

The corresponding $\delta^{13}\text{C}$ values of carbonates of the FA and FB formations are quite scattered and often negative (up to -13‰). The carbonates of the FA formation are from calcite veins or from carbonate cements of sandstones. Carbonates of the FB formation come mainly from Mn-dolomite rich black shales forming the protore of the manganese deposit of Moanda (Weber, 1968) and from the associated iron-rich level (sample 13–22). It has been shown by petrographic and geochemical evidences (Azzibrouck-Azzilez, 1986; Leclerc and Weber, 1980) that these carbonates precipitated during the early diagenesis stage in an organic-matter-rich environment and have incorporated carbon of organic origin (Gauthier-Lafaye and Weber, 1989). A same process should have occurred for the late

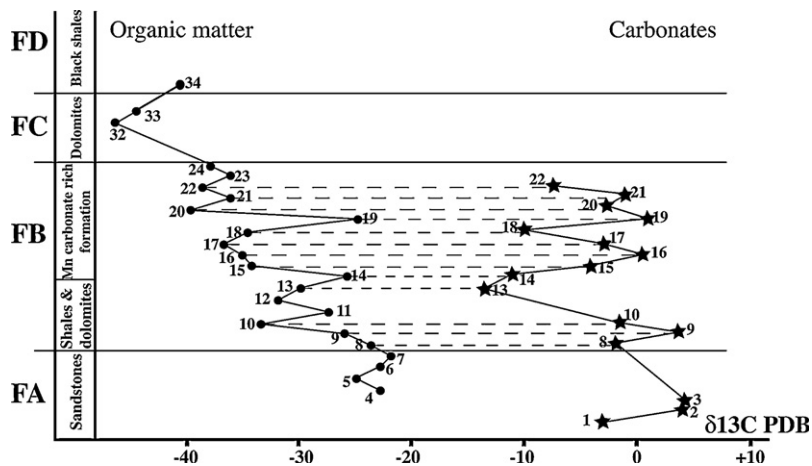


Fig. 2. Vertical distribution of the $\delta^{13}\text{C}$ values of the samples located in the central part of the Franceville basin and analyzed at the Max-Planck-Institut in Mainz. Spots: organic matter; stars: for carbonates.

Fig. 2. Distribution verticale des $\delta^{13}\text{C}$ des échantillons situés dans la partie centrale du bassin de Franceville et analysés au Max-Planck-Institut à Mayence. Points : matières organiques ; étoiles : carbonates.

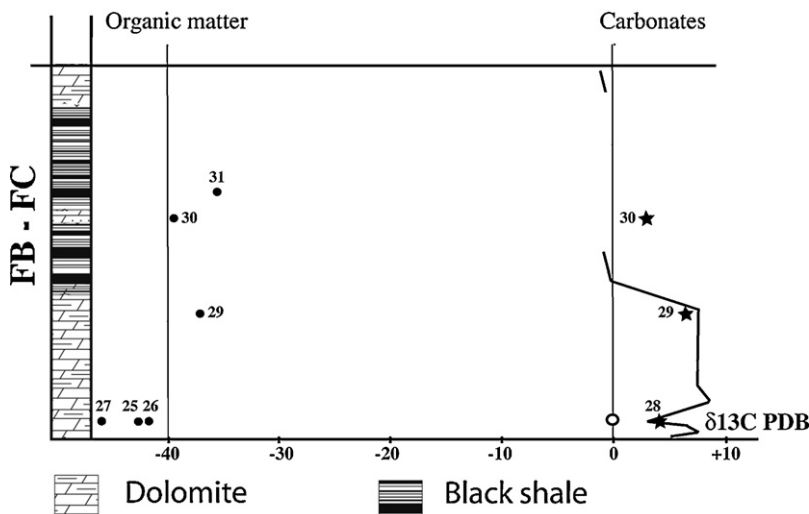


Fig. 3. Distribution of the $\delta^{13}\text{C}$ values of the samples located in the FB-C formations at the edge of the Franceville basin. The continuous line is for carbonates analyzed by Prémat et al. (2011) at Lastoursville. Data points are for analyses reported in Table 1. Black spots: organic matter; stars: dolomites; open spots: calcite in vein.

Fig. 3. Distribution verticale des $\delta^{13}\text{C}$ des échantillons situés dans la formation FB-C, en bordure du bassin de Franceville. Ligne continue : carbonates analysés par Prémat et al. (2011) à Lastoursville. Les points correspondent aux analyses reportées dans le Tableau 1. Cercle noir : matière organique ; étoile : dolomite ; cercle ouvert : calcite de veine.

carbonates i.e. the sandstone cements and calcite veins showing $\delta^{13}\text{C}$ values as low as -15‰ (Gauthier-Lafaye and Weber, 2003).

Prémat et al. (2011) gave also some isotopic analyses of Mn-dolomites from the protore of the manganese deposit, showing that the $\delta^{13}\text{C}$ values are also scattered, from -5.23 to $+6.48\text{‰}$.

3.2. Analyses of samples from the edge of the Franceville basin

At the edges of the basin, the series is condensed and it is no more possible to distinguish between the FB and FC formations. This is the case at the cliff of Lastoursville where the stratigraphic column shows a black shale layer with dolostone intercalations interbedded between two main dolomitic levels. This cross section has been described by Weber (1968) and Prémat et al. (2011). Samples from this section were analyzed both by M. Schidlowski (Table 1 and Fig. 3) and Prémat et al. (2011) (Fig. 3).

The samples 25 to 27 in Table 1 and Fig. 3 are from an open fracture filled with pyrobitumen (samples 25 and 27) and calcite (sample 26) and crosscutting the lowest dolomite layer (sample 28) of the cross section. Analyses of fluid inclusions trapped in the calcite (V. Savary and M. Pagel, not published) and of oxygen isotopes ($\delta^{18}\text{O} = -16\text{‰}$ PDB) give evidences for the occurrence of a late diagenetic event at temperatures around 200 °C . The $\delta^{13}\text{C}$ value of the calcite is slightly negative (-0.4‰), whereas it is widely positive for the dolomite ($+4.7\text{‰}$) surrounding the fracture (sample 28). Same positive values are encountered in the above dolomites, $+6.3\text{‰}$ and $+2.6\text{‰}$ (samples 29 to 31).

Results obtained by Prémat et al. (2011) show similar positive values with a maximum of $+9\text{‰}$. The trend of their data which is reproduced in Fig. 3 shows moreover a slight

decrease until negative values (-0.9‰) at the top of the section. A similar trend is also obtained by these authors on samples from the Djibalonga cliff which must be considered to be at the same stratigraphic position as the Lastoursville cliff. A positive excursion of the $\delta^{13}\text{C}$ of carbonates, up to $+9\text{‰}$ in the lower part of the section is well observed and the values decrease slowly until -2.54‰ at the top of the section (one sample). Dolomites have all been affected by diagenetic events from which new crystallizations occurred. Prémat et al. (2011) however suggest that they have almost preserved their $\delta^{13}\text{C}$ original signature. This is probably the case for the dolomites of Lastoursville and Djibalonga which are from massive layers with a low organic carbon content. Therefore, this positive excursion may correspond to the Lomagundi event (Bekker and Holland, 2012; Schidlowski et al. 1975, 1976) due to massive accumulation of organic matter in many basins over the world. The observed trend to slight negative values at the top of the sections may be interpreted as resulting from a change of dolomitic facies or, more probably, from the end of the positive excursion.

In contrast to the positive excursion of the $\delta^{13}\text{C}$ in carbonates, all the $\delta^{13}\text{C}$ values of the organic matters (pyrobitumen and kerogen) are very negative, ranging between -37 to -45‰ . It has to be pointed out here that these values are similar to those measured in the FC s.s., in the central part of the basin.

4. Comparison with Omega basin – Discussion

In drill cores from the Paleoproterozoic Omega basin (Zaonega–Shunga formation) on the southeastern margin of the Fennoscandian shield, Kump et al. (2011) observed a negative excursion of $\delta^{13}\text{C}$ in both carbonates and organic

matter with extreme values of -15‰ and -39‰ , respectively. When comparing the $\delta^{13}\text{C}$ values of the two basins, Kump et al. (2011) point out the remarkable superposition of $\delta^{13}\text{C}$ curves for organic matter, provided some adjustments of scale. Accounting for the decline in $\delta^{13}\text{C}$ values in carbonates from Lastoursville and Djibalonga cliffs, the authors suggested that this “Shunga-Francevillian negative excursion” has been global in extent, indicating massive oxidation of organic matter following the Great Oxidation Event at 2200 to 2060 Ma (Holland, 2006; Karhu and Holland, 1996). However, unlike the organic matter, the C isotopic composition of the carbonates in the Franceville and Onega basins are discordant. There is no real negative excursion in the $\delta^{13}\text{C}$ values of carbonates at Lastoursville and Djibalonga cliffs, if we exclude one negative value at the top of the Djibalonga cliff. The observed trend to slight negative values at the top of the sections may be interpreted as the end of the positive excursion of the Lomagundi event in the Franceville basin (Bekker and Holland, 2012; Schidlowski et al., 1975, 1976). This trend to slight negative values may therefore be related to the beginning of the negative excursion related in the carbonates from the Onega basin. Unfortunately, there is no carbonate in the FD formation to verify if this trend continues in the Franceville basin but the slightly different ages of the two basins is in good agreement with this hypothesis. Indeed, the Onega basin is slightly younger (1980–2090 Ma) than the Franceville basin (older than 2083 Ma) (Bros et al., 1992; Horie et al., 2005), and it can therefore record events that occurred later.

In the Franceville basin, Kump et al. compare the evolution of $\delta^{13}\text{C}$ values of organic matter located in the internal part with $\delta^{13}\text{C}$ values of carbonates located in sections representing the edges of the basin. These two sets of samples belong to the same stratigraphic levels but are definitively located in two very different environments. In the central part of the basin, the trend of the $\delta^{13}\text{C}$ values of organic matter toward negative values is correlated with the decrease of the bathymetry (Gauthier-Lafaye and Weber, 2003). However, it is remarkable to note that in the emerged environments, either in the central part of the basin or in its edges, the organic matter $\delta^{13}\text{C}$ values are similar. Therefore, it seems that the evolution of the $\delta^{13}\text{C}$ values of organic matter is more correlated with the paleogeographic position in the basin than with the stratigraphic level.

In the Francevillian basin, there is no correlation between $\delta^{13}\text{C}$ values of carbonates and $\delta^{13}\text{C}$ values of organic matter (Fig. 4). In fact, by contrast, the highest values of carbonates on the Lastoursville Cliff at the edge of the basin correspond to the lowest values of organic matter. This lack of any correlation between carbon isotopic composition of organic matter and carbonates does not argue in favor of the hypothesis proposed by Kump et al. (2011). The very negative $\delta^{13}\text{C}$ values in Francevillian organic matter published by Gauthier-Lafaye and Weber (2003) cannot be related to the massive oxidation of organic matter suggested by Kump et al. (2011) in the Onega basin.

The very negative $\delta^{13}\text{C}$ values in the organic matter associated with stromatolites and evaporitic dolomites

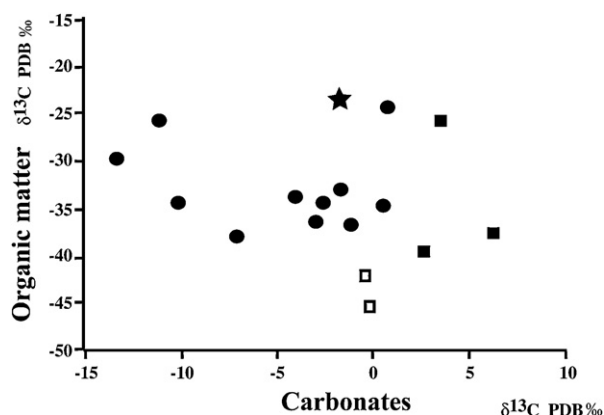


Fig. 3. $\delta^{13}\text{C}$ of organic matter versus $\delta^{13}\text{C}$ of carbonates diagram of samples analyzed at the Max-Planck-Institut in Mainz (Table 1). Black spots: black shales and dolomitic shales of the FB formation in the central part of the Franceville basin; black squares: dolomite of the FB-C formation; open squares: pyrobitumen and calcite in void in the FB-C formation at the edge of the Franceville basin; star: carbonate cement in sandstone of the FB formation.

Fig. 4. Diagramme $\delta^{13}\text{C}$ des matières organiques versus $\delta^{13}\text{C}$ des carbonates des échantillons reportés dans le Tableau 1. Cercle noir: black shales et shales dolomitiques de la formation FB du centre du bassin de Franceville; carrés blancs: pyrobitumes et calcites dans fissures de la formation FB-C en bordure du bassin de Franceville; étoile: ciment carbonate d'un grès de la formation FB.

located in the almost emerged areas at the edges of the Franceville basin lead Gauthier-Lafaye and Weber (2003) to propose the hypothesis that this negative $\delta^{13}\text{C}$ excursion could be related to the action of methanotrophic organisms which developed close to the source of oxygen (cyanobacteria of stromatolites in shallow water) by a process identical to that described by Hayes (1994) in Archean series. In the deep seawater of the stratified basin, methanogenic organisms should develop, producing a great amount of methane as it is suggested by the high organic carbon content of the FB black shales (Cortial et al., 1990). Methanotrophic organisms could also develop but could probably not consume the overall amount of methane, as it is recorded by the relatively high $\delta^{13}\text{C}$ values of the organic matter at the bottom of the FB sediments when they are compared to sediments of the same age (Schidlowski, 2001). A portion of the methane produced is discharged from the seawater to the atmosphere. Despite the presence of oxygen at a quite low concentration at that time (10% PAL) (Canfield, 2005; Kump, 2008), its residence time in the atmosphere allows it, probably, to accumulate at a fairly high rate.

Once the methane released, it can be used by the methanotrophic bacterias on the margins of the basin. In order to reach a negative isotopic anomaly in organic matter some methane must be brought into the system, otherwise the balance of the C isotopes which is controlled by the methanotrophic and methanogenic microorganisms remains stable.

When the depth of the FB basin decreases and the sediments reach the oxic zone, the production of CH_4

decreases, but the activity of the methanotrophic bacteria remains stable due to the methane accumulated in the atmosphere which causes a decrease toward more negative values of the $\delta^{13}\text{C}$ of the organic matter.

How atmospheric methane has been used by methanotrophic organisms remains uncertain. It is possible that these organisms developed close to the interface between atmosphere and seawater. However, we must also take into account the anaerobic oxidation of methane coupled primarily to sulphate reduction (Milucka et al., 2012) to explain the development of the methanotrophic organisms. In this case, it is unsuitable to call for the proximity to the source of oxygen in the almost emerged area to favor the growth of methanotrophic organisms. The occurrence of sulfate rich levels in these restricted shallow water environments (Préat et al., 2011) is in agreement with such a possibility. Sulfur isotope analyses should be performed to confirm this hypothesis.

5. Conclusion

The lack of any correlation between carbon isotopic composition of organic matter and carbonates let us to prefer the hypothesis of methanotrophic organisms action (Gauthier-Lafaye and Weber, 2003) than a massive oxidation of organic matter proposed by Kump et al. (2011) to explain the very negative $\delta^{13}\text{C}$ values in Francevillian organic matter. The Franceville's type basin was not unique, numerous similar basins should have existed at that time, resulting in the sequestration of a large amount of organic matters as it is recorded by the positive excursion of $\delta^{13}\text{C}$ in dolomites at Lastoursville and Djibalonga and other basins around the world (Lomagundi event) (Bekker and Holland, 2012). The rise of oxygen in the atmosphere is related to this event, but it is possible that the great amount of methane that accumulated in the atmosphere at a global scale 2080 Ma ago slowed down the increase of the amount of oxygen in the atmosphere and induced the end of the Lomagundi event, which probably occurred in the Francevillian at the end of the FC formation. Therefore, it is possible that the isotopic anomalies of carbon in the Onega basin is related to the oxidation of methane rather than of the organic matter.

Acknowledgements

The authors would like to thank Dr. A. Bekker and an anonymous reviewer for their very fruitful comments. Thanks also to P. Stille for his helpful comments and corrections.

References

- Azzibrouck-Azzile G. 1986. Sédimentologie et Géochimie du Francevillien (Protérozoïque inférieur). Métallogénie des gisements de manganèse de Moanda, Gabon. Thèse Univ. Louis Pasteur of Strasbourg, France. 214 p.
- Bekker, A., Holland, H.D., 2012. Oxygen overshoot and recovery during the Early Paleoproterozoic. *Earth Planet. Sci. Lett.* 317, 295–304.
- Bekker, A., Holland, H.D., Wang, P.L., Rumble, D., Stein, H.J., Hannah, J.L., Coetzee, L.L., Beukes, N.J., 2004. Dating the rise of atmospheric oxygen. *Nature* 427, 117–120.
- Bertrand-Sarfati, J., Potin, B., 1994. Microfossiliferous cherty stromatolites in the 2000 Ma Franceville Group. *Gabon Precamb. Res.* 65, 341–356.
- Bros, R., Stille, P., Gauthier-Lafaye, F., Weber, F., Clauer, N., 1992. Sm-Nd isotopic dating of Proterozoic clay material. Example from Francevillian sedimentary Series (Gabon). *Earth Planet. Sci. Lett.* 113, 207–218.
- Canfield, D.E., 2005. The early history of atmospheric oxygen: homage to Robert M. Garrels. *Ann Earth Rev. Planet Sci.* 33, 1–36.
- Cortial, F., Gauthier-Lafaye, F., Oberlin, A., Lacrampe-Couloume, G., Weber, F., 1990. Characterization of organic matter associated with uranium deposits in the Francevillian Formation of Gabon (Lower Proterozoic). *Organ. Geochem.* 15, 73–85.
- El Albani, A., Bengton, S., Canfield, D.E., Bekker, A., Miacchiarelli, R., Mazurier, A., Hammarlund, E.U., Boulvais, P., Dupuy, J.J., Fontaine, C., Füsi, F.T., Gauthier-Lafaye, F., Janvier, P., Javaux, E., Ossa-Ossa, F., Pierson-Wickmann, A.C., Riboulleau, A., Sardini, P., Vachard, D., Whitehouse, M., Meunier, A., 2010. Large colonial organisms with coordinated growth in oxygenated environments 2.1 billion years ago. *Nature* 466, 100–104.
- Favre-Mercure, R., 1965. Contribution à l'étude sédimentologique et géochimique du bassin de Franceville (Gabon). D.E.S. Univ. Strasbourg, France, 127 pp.
- Feybesse, J.L., Johan, V., Triboulet, C., Guerrot, C., Mayaga-Mikolo, F., Bouchot, V., Eko N'dong, J., 1998. The West Central African belt: a model of 2.5–2.0 Gga accretion and two-phase orogenic evolution. *Precamb. Res.* 87, 161–216.
- Gauthier-Lafaye, F., 1986. Les gisements d'uranium du Gabon et les réacteurs d'Oklo. Modèle métallogénique de gites à fortes teneurs du Protérozoïque inférieur. *Mem. Sci. Geol.* 78, 206.
- Gauthier-Lafaye, F., Weber, F., 1989. The Francevillian (Lower Proterozoic) uranium ore deposits of Gabon. *Econ. Geol.* 84, 2267–2285.
- Gauthier-Lafaye, F., Weber, F., 2003. Natural nuclear fission reactors: time constraints for occurrence and their relation to uranium and manganese deposits and to the evolution of the atmosphere. *Precamb. Res.* 120, 81–101.
- Gauthier-Lafaye, F., Weber, F., Ohmoto, H., 1989. Natural fission reactors of Oklo. *Econ. Geol.* 84, 2286–2295.
- Hayes, J.M., 1994. Global methanotrophy at the Archean-Proterozoic transition. *Early Life on Earth. Nobel Symposium.* Columbia University Press, New-York, 220–36.
- Holland, H.D., 2006. The Oxygenation of Atmosphere and Oceans. *Philos. Trans. R. Soc. Lond. Ser. B* 361, 903–915.
- Horie, K., Hidaka, H., Gauthier-Lafaye, F., 2005. U-Pb geochronology and geochemistry of zircon from the Franceville series at Bidoudouma. *Gabon Geochim. Cosmochim. Acta* 69 (10), A11.
- Karhu, J.A., Holland, H.D., 1996. Carbon isotopes and the rise of atmospheric oxygen. *Geology* 24, 670–677.
- Kump, L.R., 2008. The rise of atmospheric oxygen. *Nature* 451, 277.
- Kump, L.R., Junium, C., Arthur, M.A., Brasier, A., Fallick, A., Melezhik, V., Lepand, A., Crne, A.E., Luo, G., 2011. Isotopic evidence for massive oxidation of organic matter following the Great Oxidation Event. *Science* 334, 1694–1696.
- Leclerc, J., Weber, F., 1980. Geology and genesis of the Moanda manganese deposits, Republic of Gabon. *Proc. XXVth Intern. Congr. Geology, Sydney (1976)*. In: Varensov, I.M., Gaassell, G.Y. (Eds.), *Geology and geochemistry of manganese*, 2. Schweitzerbart'sche Verl. Stuttgart, pp. 89–109.
- Milucka, J., Ferdelman, T., Polerecky, L., Franzke, D., Wegener, G., Schmid, M., Lieberwirth, I., Wagner, M., Widdel, F., Kuypers, M., 2012. Zero-valent sulphur is a key intermediate in marine methane oxidation. *Nature* 491, 541–546.
- Mossmann, D.J., Gauthier-Lafaye, F., Jackson, S.E., 2005. Black shales, organic matter, ore genesis and hydrocarbon generation in the Paleoproterozoic Franceville series, Gabon. *Precamb. Res.* 137, 253–272.
- Neuilly, M., Bussac, J., Fréjacques, C., Nief, G., Vendryes, G., Yvon, J., 1972. Sur l'existence dans un passé reculé d'une réaction en chaîne naturelle de fission, dans le gisement d'uranium d'Oklo (Gabon). *C. R. Acad. Sci. Paris, Ser. D* 275, 1847–1849.
- Préat, A., Bouton, P., Thiéblemont, D., Prian, J.-P., Ndongze, S.S., Delpomdor, F., 2011. Paleoproterozoic high $\delta^{13}\text{C}$ dolomites from the Lastoursville and Franceville basins (SE Gabon): Stratigraphic and syndensimentary subsidence implications. *Precamb. Res.* 189, 212–228.
- Schidlowski, M., 2001. Carbon isotopes as biochemical recorders of life over 3.8 Ga of earth history: evolution of a concept. *Precamb. Res.* 106, 117–134.
- Schidlowski, M., Richmann, R., Junge, C.E., 1975. Precambrian Sedimentary Carbonates: carbon and oxygen isotope geochemistry and

- implications for the terrestrial oxygen budget. *Precamb. Res.* 2, 1–69.
- Schidlowski, M., Richmann, R., Junge, C.E., 1976. Carbon isotope geochemistry of the Precambrian Lomagundi carbonate province. Rhodesia. *Geochim. Cosmochim. Acta* 40, 440–445.
- Thiéblemont, P., Castaing, C., Billa, M., Bouton, P., Peéat, A., 2009. Notice explicative de la carte géologique et des ressources minérales de la République Gabonaise au 1/1000 000. Éditions BRGM – Ministère des Mines, des Hydrocarbures, Libreville, 381 p.
- Weber, F., 1968. Une série précambrienne du Gabon : le Francevillien. *Sédimentologie, géochimie et relation avec les gîtes minéraux associés*. Mem. Serv. Carte Geol. Als. Lorr. 28, 328.
- Weber, F., 1997. Evolution of lateritic manganese deposits. In: Paquet, H., Clauer, N. (Eds.), *Soils and sediments, Mineralogy and Geochemistry*. Heidelberg, Springer, pp. 97–124.
- Weber, F., Schidlowski, M., Arneeth, J.D., Gauthier-Lafaye, F., 1983. Carbon isotope geochemistry of the Lower Proterozoic Francevillian series of Gabon (Africa). *Terra Cognita* 3, 220.