

## MICROSPHERULES FROM THE GIVET LIMESTONE IN THE GIVETIAN HISTORICAL TYPE AREA (ARDENNES, FRANCE): DESCRIPTION AND SIGNIFICANCE

### *Des microsphérules dans le Calcaire de Givet de la région-type historique du Givétien (Ardenne, France) : description et signification*

par Sébastien MAILLET (\*, \*\*) & Bruno MILHAU (\*\*)

**Abstract.** – For the first time around the world, glassy and ferrous microspherules associated with glass-like carbon elements are reported in the Givetian. Three levels providing microspherules are described herein, located in the Trois-Fontaines, Terres d'Hauts and Fromelennes formations in the Givet historical type-area (Ardennes). A total of 142 spherules have been extracted from these three levels. With an average diameter of 350  $\mu\text{m}$ , they exhibit a large panel of forms and colours. Chemical quantifications and cartographies performed under ESEM and electronic microprobe show that silica, aluminium and iron are the main components. In detail, microspherules show diverse chemical compositions; some of them show micro-inclusions chemically different of the glass-matrix, internal vesicles or also a heterogeneous glass matrix. The natural origin of these microspherules is established and their formation(s) – volcanism vs. impact – is discussed. Moreover, the spherules show several features of microtektites and their association with glass-like carbon may be evidence for several asteroid impacts during the Givetian. As singular and instantaneous deposits on wide areas, these levels should be excellent chronostratigraphic tools useful for superregional to global correlations.

**Résumé.** – Pour la première fois à travers le monde, des microsphérules vitreuses et ferreuses associées à des éléments de carbone vitrifiés sont signalées dans le Givétien. Trois niveaux centimétriques fournissant des microsphérules sont décrits dans cette étude, localisés au sein des formations givétiennes des Trois-Fontaines, des Terres d'Hauts et de Fromelennes dans la région-type historique de Givet (Ardennes). Au total, 142 microsphérules ont été extraites pour ces trois niveaux. D'un diamètre moyen de 350  $\mu\text{m}$ , elles présentent un grand panel de formes et de couleurs. Des quantifications et cartographies chimiques, effectuées au MEB et à la microsonde électronique, mettent en avant que la silice, l'aluminium et le fer sont les éléments chimiques globalement dominants. Dans le détail, les microsphérules présentent des compositions chimiques diversifiées et certaines montrent également des inclusions de nature chimique différente de la matrice les contenant, des vésicules ou encore une matrice chimiquement hétérogène. Le caractère naturel de ces microsphérules est établi et leur(s) origine(s) – volcanisme ou impact – est discutée. De plus, les sphérules possèdent des caractéristiques de microtektites et leur association avec du carbone vitrifié pourrait être la preuve de plusieurs impacts extraterrestres durant le Givétien. En tant que dépôts particuliers et instantanés sur de grandes étendues géographiques, ces niveaux pourraient constituer un puissant outil chronostratigraphique utile pour des corrélations suprarégionales à globales.

**Key words.** – Middle Devonian, glassy microspherules, glass-like carbon, instantaneous deposit, impact.

**Mot-clés.** – Dévonien moyen, microsphérules vitreuses, carbone vitrifié, dépôt instantané, impact.

### I. – INTRODUCTION

Microspherules are unusual deposits through the geological record. Their origin and significance, although often difficult to determine precisely, have to be questioned since they can be either natural (biological or mineral) or an artificial product. Especially, if natural and mineral, microspherules can be the witness of punctual outstanding phenomena as volcanism or impact. The main purpose of this paper is to report the presence of glassy and ferrous microspherules in three levels from Lower and Middle Givetian carbonate deposits of the Givetian historical stratotype area (Givet, Ardennes, France). Furthermore, if the Givetian is a period of environmental changes punctuated by several biotic events and crisis (House, 2002; Boulvain *et al.*, 2009; Maillet, 2013), aim of this paper is not to argue for a

doubtful relation between the presence of such microspherules and Givetian events, but is only to describe the material and to discuss about its possible origin.

Despite numerous geological studies made in Ardenne for two hundred years, this is the first time that microspherules are reported in Givetian deposits of this area. However, microtektites have been found around the Frasnian/Famennian boundary in Hony and Senzeille areas (Claeys & Casier, 1994; Claeys *et al.*, 1992). So far, except microtektites found at the Eifelian/Givetian boundary in Morocco (Ellwood *et al.*, 2003; Schmitz *et al.*, 2006) and at the Givetian/Frasnian boundary in North America (Isachsen, 1998), no work has reported microspherules within Givetian deposits around the world.

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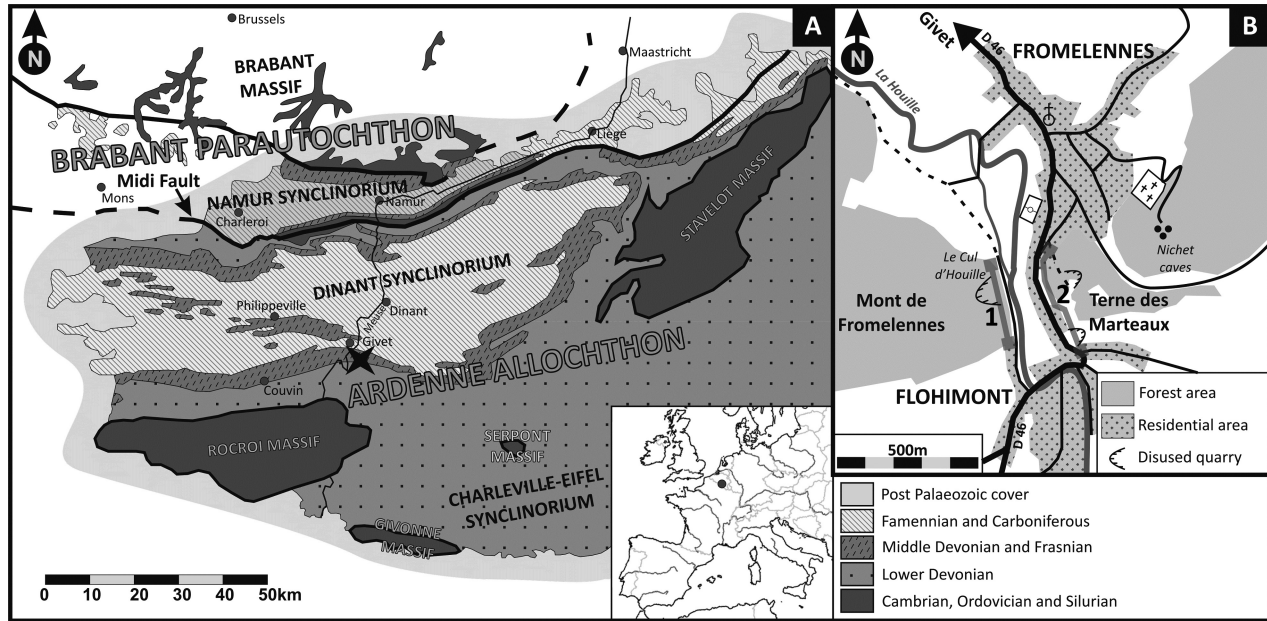


Fig. 1. – Geological and geographical settings. A: Ardenne structural units (adapted from Bultynck, 2001). The dark star indicates the Fromelennes area; B: Location map of the studied sections (1: Cul d'Houille section; 2: Flohimont section).

Fig. 1. — Contextes géologique et géographique. A : Unités structurales de l'Ardenne (modifié d'après Bultynck, 2001). L'étoile noire indique la région de Fromelennes ; B : Carte de situation des coupes étudiées (1 : coupe du Cul d'Houille ; 2 : coupe de Flohimont).

## II. – GEOGRAPHICAL AND GEOLOGICAL SETTINGS

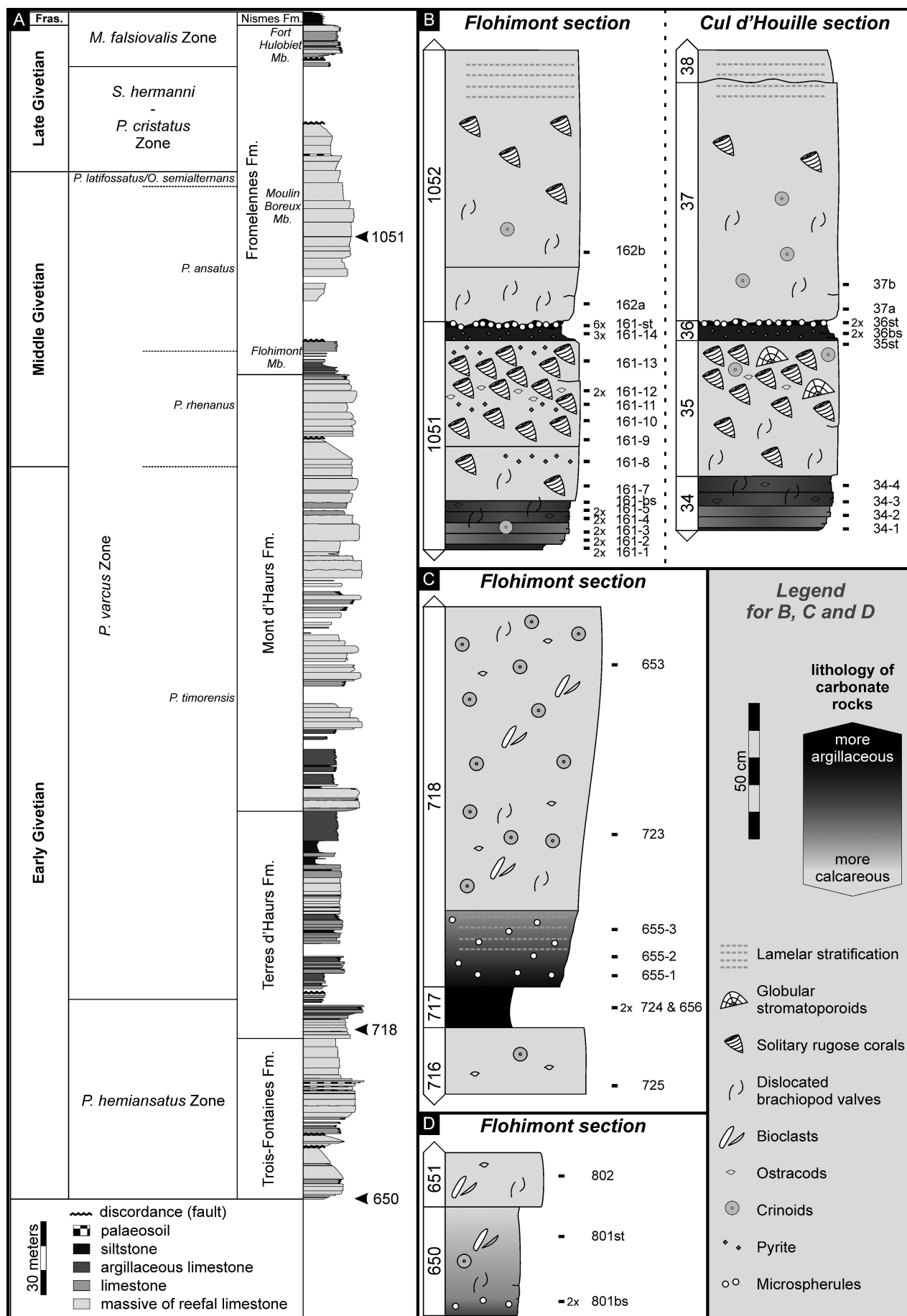
The Givet area (Ardennes, France) is the historical stratotype for the Givetian geological stage. It belongs to the southern border of the Dinant Synclinorium (Ardenne Allochthon; Fig. 1A). In this area, the Givetian is exposed through a 500 m-thick carbonate sequence. This sequence encompasses the upper part of the Hanonet Formation (Fm.), the entire Givet Group (Trois-Fontaines Fm., Terres d'Haus Fm., Mont d'Haus Fm.

and Fromelennes Fm.) and the extreme base of the Nismes Formation. Two sections near Fromelennes, few kilometres southwards to Givet, have been studied. The Flohimont section, along the road D46 between Fromelennes and Flohimont, is located eastwards to the Houille River (Fig. 1B); the Givet Group and the base of the Nismes Fm. are particularly well exposed in this outcrop (Fig. 2A; Boulvain *et al.*, 2009; Maillet, 2013). The Cul d'Houille section is located along the western bank of the Houille river (Fig. 1B); the upper part of the Mont

Fig. 2. – The microspherule levels. A: Synthetic stratigraphical column of the Flohimont section. The three microspherules-bearing beds (650, 718 and 1051) are indicated. The conodont zonation is adapted from Gouwy & Bultynck (2003). B: Detail of the microspherule level of the Moulin Boreux Member (Fromelennes Formation) in the Flohimont and the Cul d'Houille sections. Bed 1051 in the Flohimont section is a fine grained-limestone sometimes slightly dolomitized. It can be subdivided into three parts, correlated to the beds 34, 35 and 36 of Hubert & Pinte (2009) in the Cul d'Houille section. The basal part overlies a brown clayey seal and shows a plate-splitting argillaceous limestone with rare crinoids, disarticulated brachiopod valves and small fluorine crystals. The median part shows a massive grey dolomitized limestone with abundant badly preserved rugose corals, disarticulated brachiopod valves, ostracods (*Cryptophyllus* sp. 3 *sensu* Magne, 1964) and small pyrite crystals. The top part is relatively thin and shows a dark and argillaceous limestone with abundant small pyrite and fluorine crystals, overlain by a black clayey seal of variable thickness (some mm to some cm) containing microspherules. C: Detail of the microspherule level of the Terres d'Haus Formation in the Flohimont section. Bed 718 in the Flohimont section is located some metres above the basal biostrome defining the base of the Terres d'Haus Formation. Overlying a 20 cm-thick dark clayey level, the basal part of the bed 718 is a 30 cm-thick argillaceous limestone containing microspherules. It is overlain by a more massive, dolomitized and bioclastic limestone of about 1 m-thick providing abundant crinoids. D: Detail of the microspherule level of the Trois-Fontaines Formation in the Flohimont section. Bed 650 is the first bed of the Flohimont section. This 40 cm-thick dolomitized limestone, slightly bioclastic, exhibits a more argillaceous basal part which contains microspherules.

Fig. 2. — Les niveaux à microsphérules. A: Colonne stratigraphique synthétique de la coupe de Flohimont. Les trois bancs à microsphérules (650, 718 et 1051) sont indiqués. La biozonation à conodontes est adaptée de Gouwy & Bultynck (2003). B: Détail du niveau à microsphérules du Membre du Moulin Boreux (Formation de Fromelennes) dans les coupes de Flohimont et du Cul d'Houille. Le banc 1051 de la coupe de Flohimont se présente sous la forme d'un calcaire à grain fin parfois légèrement dolomitique. Ce banc peut être divisé en trois parties, corrélées aux bancs 34, 35 et 36 de Hubert & Pinte (2009) de la coupe du Cul d'Houille. La partie basale, surmontant un joint argileux marron, montre un calcaire argileux à débit en plaquettes, fournissant de rares crinoïdes, des valves désarticulées de brachiopodes et de petits cristaux de fluorine. La partie médiane se caractérise par un calcaire dolomitisé massif gris, contenant d'abondants coraux rugueux mal préservés, des valves désarticulées de brachiopodes, des ostracodes (*Cryptophyllus* sp. 3 *sensu* Magne, 1964) et de petits cristaux de pyrite. La partie supérieure est relativement peu épaisse et montre un calcaire argileux sombre avec d'abondants petits cristaux de pyrite et de fluorine, surmonté par un joint argileux noir d'épaisseur variable (quelques mm à quelques cm) contenant d'abondantes microsphérules. C : Détail du niveau à microsphérules de la Formation des Terres d'Haus dans la coupe de Flohimont. Le banc 718 de la coupe de Flohimont est situé quelques mètres au dessus du biostrome définissant la base de la Formation des Terres d'Haus. Située immédiatement au dessus d'un niveau argileux sombre d'environ 20 cm d'épaisseur, la partie basale du banc 718 est un calcaire argileux d'environ 30 cm d'épaisseur, contenant des microsphérules. Celle-ci est surmontée d'un calcaire dolomitisé plus massif et bioclastique, d'environ 1 m d'épaisseur et fournissant d'abondant crinoïdes. D : Détail du niveau à microsphérules de la Formation des Trois-Fontaines dans la coupe de Flohimont. Le banc 650 constitue le premier banc de la coupe de Flohimont. Il d'agit d'un calcaire dolomitisé légèrement bioclastique, d'environ 40 cm, dont la partie basale, plus argileuse, fournit des microsphérules.





d'Haus Fm. and the Fromelennes Fm. are exposed (Hubert & Pinte, 2009; Maillet, 2013). Both sections are stratigraphically complementary (Maillet *et al.*, 2011, 2013) and expose the Fromelennes Fm. stratotype (Bultynck *et al.*, 1991).

In the Fromelennes area, the base of the Givetian is missing and the carbonate sequence begins with the Trois-Fontaines Fm., with a faulted base. Thick dolomitized limestones (beds frequently thicker than 1 metre) and some palaeosoils characterize this 60 m-thick formation. Then, a metre-thick biostromal bed with abundant *Pachyfavosites polymorphus* (Goldfuss, 1829) indicates the base of the Terres d'Haus Fm., a 80 m-thick formation composed of thin argillaceous limestones beds alternating with some dolomitized limestones. Above, a thick biostrome with abundant *Heliolites* Dana, 1846 tabulate corals defines the base of the Mont d'Haus Fm., a 180 m-thick formation exposing an alternation of thin argillaceous beds and massive reefal limestones and biostromes. It is overlain by the 140 m-thick Fromelennes Fm., subdivided into three 'members': the Flohimont Member (30 m of argillaceous limestones), the Moulin Boreux Member (85 m of massive dolomitic and reefal limestones) and the Fort Hulobiet Member (25 m of argillaceous and nodular limestones). The first bed of the Fromelennes Fm. is a brachiopod coquina argillaceous limestone (Maillet *et al.*, 2010). Finally, siltstones providing large-sized brachiopods (= 'Zone des Monstres' of Gosselet, 1871) belong to the base of the Nismes Fm.

A conodont biozonation has been precisely established in the Givet area by Gouwy & Bultynck (2003). However, the Givetian-Frasnian boundary is still discussed by the Subcommittee on Devonian Stratigraphy. Based on the Frasnian Event, this boundary was originally defined by the first occurrence of *Ancyrodella rotundiloba rotundiloba* (Klapper *et al.*, 1987). Currently, some authors place this boundary lower, at the first occurrence of the genus *Ancyrodella* (with *A. soluta*, *A. pristina*, *A. binodosa*), coinciding with the middle part of the lower *Mesotaxis falsiovalis* Zone (Casier & Pr  at, 2007; Gouwy & Bultynck, 2003; Narkiewicz & Bultynck, 2010; Tsyganko, 2009). We take into consideration this new definition here: in the Fromelennes area, *A. binodosa* is known at the base of the Nismes Fm. while *A. rotundiloba rotundiloba* appears 1 m above (Bultynck, 1974; Bultynck & Coen, 1982).

### III. – MATERIAL AND METHODS

#### 1) Sampling and collected material

A bed by bed sampling was performed in the two studied sections, with 532 samples collected throughout the entire Givetian carbonate sequences. Initially, each rock sample was processed using the hot acetolysis method (Crasquin-Soleau *et al.*, 2005; Lethiers & Crasquin, 1988; Milhau, 1984) in order to analyze microfaunas, and especially ostracods (see Maillet, 2013; Maillet *et al.*, 2013). After a sorting under binocular lens, four samples among the 532 provided microspherules: samples 161st (Fig. 2B), 655 (Fig. 2C) and 801bs (Fig. 2D), respectively corresponding to the beds 1051, 718 and 650 in the Flohimont section (Fig. 2A), and sample 36st, corresponding to the bed 36 in the Cul d'Houille section (see Fig. 2B; Hubert & Pinte, 2009; Maillet, 2013). Then, about 40 additional samples were collected at different levels of these four beds to localize more precisely the microspherules (see description of horizons below) and to get more material. These new samples were attacked with chlorhydric acid.

A total of 142 microspherules has been extracted. Most of them show a perfect spherical shape with a smooth glassy surface. Their sizes range from 140 to 620 µm in diameter. The largest part of the microspherules is colourless and transparent, with an average-diameter of 350 µm; their shape is frequently spherical, but also sometimes more tubular, bispherical or tear-dropped (Fig. 3); small protrusions are often observed on the surface; broken surfaces are conchoidal; they are isotropic under polarized light; they show small internal vesicles and more rarely micro-inclusions (tubular forms). Other microspherules of smaller size (average-diameter of about 200 µm) show a large panel of colours (see description of horizons below), and are translucent to opaque, showing glassy to crystallized surface (Fig. 3). Abundant mm-sized glass-like carbon elements have been retrieved associated to the microspherules; these elements are brightness, grey to black and display a spongy-aspect (Fig. 3).

#### 2) Description of the microspherules levels

##### a) The Trois-Fontaines Formation level

The first microspherules level is located in the lower part of the Trois-Fontaines Fm. in the Flohimont section (level 650 in Fig. 2A). The level belongs to the middle part of the *Polygnathus hemiansatus* conodont Zone (Lower Givetian). Two samples were collected in the base of the first bed (bed 801bs in Fig. 2D; see also Maillet, 2013), a 40 cm-thick slightly argillaceous and dolomitic limestone. Twelve microspherules (Fig. 3) were retrieved from about 100 g of rock: most of them are transparent and colourless with a smooth or slightly pitted surface and they display spherical, spheroid or bispherical shapes, sometimes with protrusions; one spherical microspherule is opaque, grey and exhibits a crystallized surface. Abundant glass-like carbon elements are associated to these microspherules.

##### b) The Terres d'Haus Formation level

The second microspherules level is located in the lower part of the Terres d'Haus Fm. in the Flohimont section (level 718 in Fig. 2A). It crops out along the road D46. The level belongs to the upper part of the *P. hemiansatus* Zone (Lower Givetian). Three samples (about 250 g of rock) from the argillaceous basal part of the bed 718 (samples 655 in Fig. 2C; see also Maillet, 2013) provided 24 microspherules and glass-like carbon (Fig. 3). The microspherules consequently appear to be dispersed in the basal part of this bed. They display different colours and shapes: 20 spherules display a glassy surface, sometimes pitted and among them, 11 are transparent (5 spherical, 5 tubular, 1 tear drop-shaped) and 9 are translucent (2 dark brown and spherical, 1 red and spherical, 2 light yellow and elongate, 4 black and spherical); 4 microspherules are opaque and spherical (1 grey-brownish and 3 grey with a crystallized surface).

##### c) The Fromelennes Formation level

The third microspherules level is located in the lower part of the Moulin Boreux Member in the Fromelennes Fm., both in the Flohimont (level 1051 in Fig. 2A) and in the Cul d'Houille (level 36 in Fig. 2B) sections. The level belongs to the *Polygnathus ansatus* conodont subzone (middle *Polygnathus varcus* conodont Zone, late Middle Givetian). In the two sections, the microspherules-bearing level is a very thin and irregular dark clayey seal, quite difficult to sample. In the Flohimont section, on 30 samples from the bed 1051 and the base of the bed 1052, 6 come from the dark clayey seal between

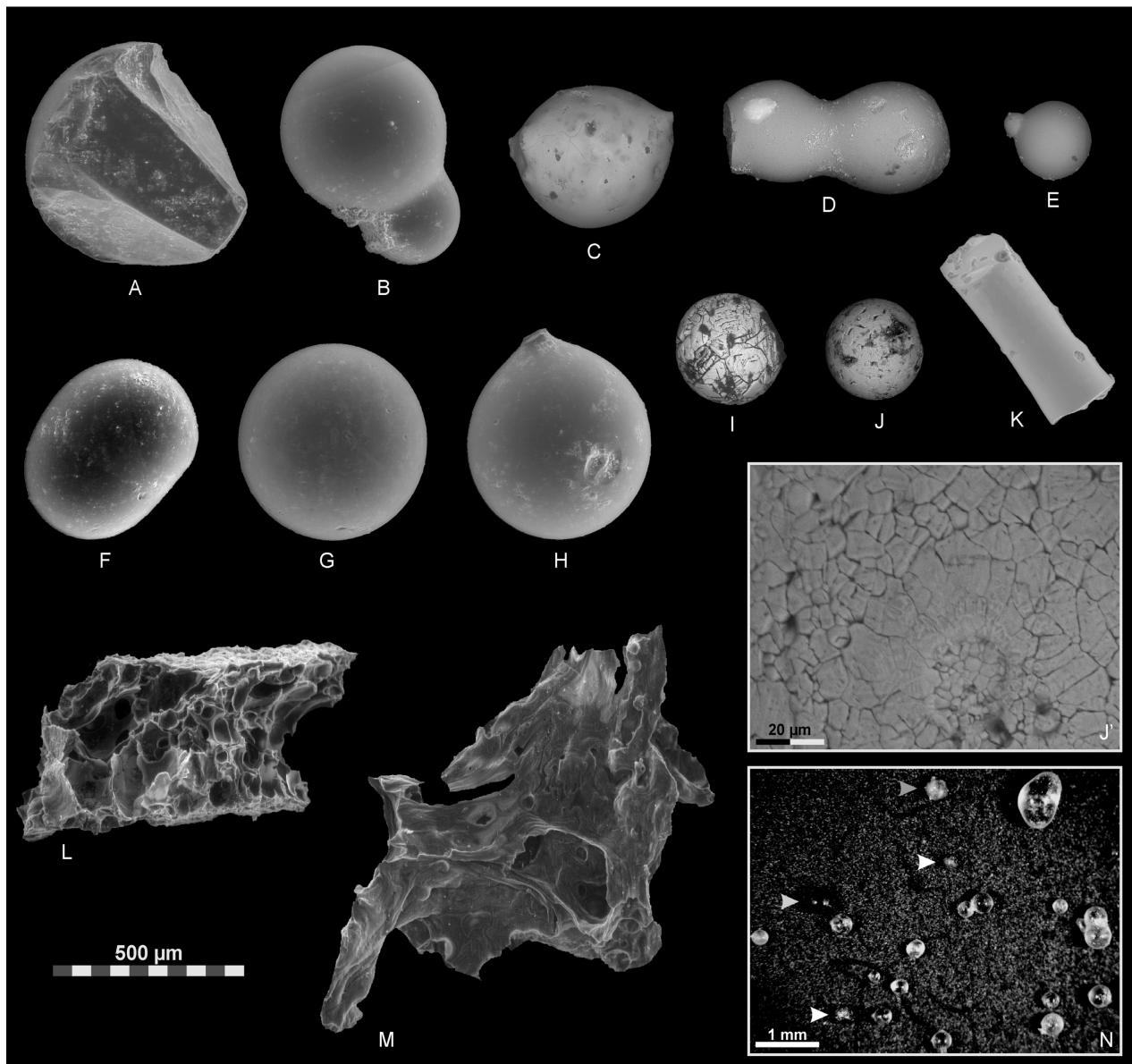


Fig. 3. — Some microspherules and glass-like carbon elements from the Givetian of the Fromelennes area. A-M: ESEM pictures. A: spherical colourless microspherule from bed 1051 showing a conchoidal broken surface, C.O.F.L.S. 1161; B: bispherical colourless microspherule from bed 1051, C.O.F.L.S. 1162; C: spheroid dark brown microspherule from bed 718, C.O.F.L.S. 1163; D: bispherical colourless microspherule from bed 1051, C.O.F.L.S. 1164; E: spherical red microspherule from bed 718 with protrusion, C.O.F.L.S. 1165; F: ovoidal colourless microspherule from bed 1051 showing a potassium-depleted zone (slightly darker zone at top right), C.O.F.L.S. 1166; G: spherical colourless microspherule from bed 718, C.O.F.L.S. 1167; H: spherical colourless microspherule from bed 1051 with a pitted surface and a protrusion, C.O.F.L.S. 1168; I-J: spherical grey and brightness microspherules from bed 1051, C.O.F.L.S. 1169 and 1170; J': detail of the crystallized surface of the microspherule J; K: broken tubular colourless microspherule from bed 718, C.O.F.L.S. 1171; L-M: glass-like carbon elements from bed 718, C.O.F.L.S. 1172 and 1173. N: Optical photography under binocular lens (bed 1051). Most of the microspherules are transparent and colourless. Grey arrow at top-centre indicates a yellow translucent microspherule; grey arrow at left-centre points a brown translucent microspherule; white arrows show grey opaque brightness microspherules.

Fig. 3. — Quelques microsphérules et éléments de carbone vitrifié du Givétien de la région de Fromelennes. A-M : clichés au MEB. A : microsphérule sphérique incolore montrant une cassure conchoïdale, banc 1051, C.O.F.L.S. 1161 ; B : microsphérule bi-sphérique incolore, banc 1051, C.O.F.L.S. 1162 ; C : microsphérule sphéroïdale marron foncé, banc 718, C.O.F.L.S. 1163 ; D : microsphérule bi-sphérique incolore, banc 1051, C.O.F.L.S. 1164 ; E : microsphérule sphérique rouge avec protubérance, banc 718, C.O.F.L.S. 1165 ; F : microsphérule ovoïde incolore montrant une zone appauvrie en potassium (zone légèrement plus foncée en haut à droite), banc 1051, C.O.F.L.S. 1166 ; G : microsphérule sphérique incolore, banc 718, C.O.F.L.S. 1167 ; H : microsphérule sphérique incolore montrant une surface piquetée et une protubérance, banc 1051, C.O.F.L.S. 1168 ; I-J : microsphérules sphériques grises brillantes, banc 1051, C.O.F.L.S. 1169 et 1170 ; J' : détail de la surface cristallisée de la microsphérule J ; K : Microsphérule tubulaire incolore cassée, banc 718, C.O.F.L.S. 1171 ; L-M : éléments de carbone vitrifié, banc 718, C.O.F.L.S. 1172 et 1173. N : Photographie de microsphérules sous loupe binoculaire (banc 1051). La plupart des microsphérules sont incolores et transparentes. La flèche grise en haut au centre indique une microsphérule jaune et translucide ; la flèche grise à gauche au centre montre une microsphérule marron et translucide ; les flèches blanches montrent deux microsphérules grises, brillantes et opaques.

| Sample type                                                              | Type 1<br>Colourless<br>transparent<br>microspherules | Type 2<br>Grey<br>opaque<br>microspherules | Type 3<br>Yellow, red<br>and brown<br>translucent<br>microspherules | Type 4<br>Black<br>translucent<br>microspherules | Type 5<br>Grey-brownish<br>opaque<br>microspherules | Type 6<br>Colourless<br>transparent<br>tubular<br>microspherules | Glass-like<br>carbon<br>elements * | Artificial<br>microbeads             |
|--------------------------------------------------------------------------|-------------------------------------------------------|--------------------------------------------|---------------------------------------------------------------------|--------------------------------------------------|-----------------------------------------------------|------------------------------------------------------------------|------------------------------------|--------------------------------------|
| Quantity of<br>samples                                                   | 8                                                     | 3                                          | 6                                                                   | 1                                                | 1                                                   | 1                                                                | 3                                  | 4                                    |
| Number of<br>measurements                                                | 23                                                    | 27                                         | 28                                                                  | 5                                                | 8                                                   | 4                                                                | 12                                 | 8                                    |
| Al <sub>2</sub> O <sub>3</sub>                                           | 1.11<br>(0.68-2.68)                                   | 0.34<br>(0-2.82)                           | <b>15.55</b><br><b>(9.82-38.92)</b>                                 | <b>25.44</b>                                     | <b>21.47</b>                                        | <b>11.60</b>                                                     | <b>4.98</b>                        | 1.06<br>(0.91-1.16)                  |
| SiO <sub>2</sub>                                                         | <b>73.45</b><br><b>(63.87-80.11)</b>                  | 0.98<br>(0-3.87)                           | <b>59.22</b><br><b>(38.79-65.28)</b>                                | <b>50.20</b>                                     | <b>31.70</b>                                        | <b>33.89</b>                                                     | <b>8.01</b>                        | <b>69.46</b><br><b>(68.62-70.46)</b> |
| Na <sub>2</sub> O                                                        | 5.88<br>(1.73-9.34)                                   | 0.09<br>(0-0.95)                           | 0.78<br>(0.36-1.48)                                                 | 0.58                                             | 0.42                                                | <LD                                                              | <LD                                | <b>14.06</b><br><b>(12.75-15.25)</b> |
| MgO                                                                      | 4.06<br>(3.44-5.1)                                    | 0.07<br>(0-0.62)                           | 1.49<br>(0.87-4.23)                                                 | 3.92                                             | 3.86                                                | 9.28                                                             | <LD                                | 4.38<br>(4.23-4.67)                  |
| K <sub>2</sub> O                                                         | 0.27<br>(0.06-1.74)                                   | <LD                                        | <b>3.02</b><br><b>(1.21-15.28)</b>                                  | 2.03                                             | 1.51                                                | <LD                                                              | 0.73                               | <LD                                  |
| CaO                                                                      | <b>10.07</b><br><b>(7.69-13.52)</b>                   | <LD                                        | 3.36<br>(0.45-10.81)                                                | <b>10.76</b>                                     | 6.63                                                | <b>37.95</b>                                                     | <LD                                | <b>10.59</b><br><b>(10.3-10.85)</b>  |
| Fe <sub>2</sub> O <sub>3</sub>                                           | 0.17<br>(0-1.17)                                      | <b>91.69</b><br><b>(88.1-96.3)</b>         | <b>7.59</b><br><b>(2.34-15.94)</b>                                  | 2.43                                             | <b>32.42</b>                                        | 5.06                                                             | <LD                                | <LD                                  |
| SO <sub>4</sub>                                                          | 0.31<br>(0.26-0.84)                                   | <LD                                        | <LD                                                                 | <LD                                              | <LD                                                 | 1.63                                                             | 1.50                               | <LD                                  |
| Ni                                                                       | <LD                                                   | <LD                                        | <LD                                                                 | <LD                                              | <LD                                                 | <LD                                                              | <LD                                | <LD                                  |
| CuO                                                                      | <LD                                                   | <LD                                        | <LD                                                                 | <LD                                              | <LD                                                 | <LD                                                              | <LD                                | <LD                                  |
| TiO <sub>2</sub>                                                         | <LD                                                   | <LD                                        | 1.04<br>(0.35-2.52)                                                 | 1.04                                             | 0.88                                                | 0.95                                                             | <LD                                | <LD                                  |
| Cr <sub>2</sub> O <sub>3</sub>                                           | <LD                                                   | <LD                                        | <LD                                                                 | <LD                                              | <LD                                                 | <LD                                                              | <LD                                | <LD                                  |
| MnO                                                                      | <LD                                                   | 0.17<br>(0-0.75)                           | <LD                                                                 | <LD                                              | <LD                                                 | <LD                                                              | <LD                                | <LD                                  |
| PbO                                                                      | <LD                                                   | <LD                                        | <LD                                                                 | <LD                                              | <LD                                                 | <LD                                                              | <LD                                | <LD                                  |
| K <sub>2</sub> O/Na <sub>2</sub> O                                       | 0.05                                                  | 0.00                                       | 3.88                                                                | 3.51                                             | 3.60                                                | -                                                                | -                                  | -                                    |
| Al <sub>2</sub> O <sub>3</sub> /(Na <sub>2</sub> O+<br>K <sub>2</sub> O) | 0.18                                                  | 3.92                                       | 4.10                                                                | 9.75                                             | 11.12                                               | -                                                                | -                                  | 0.07                                 |
| R Al                                                                     | 5.10                                                  | 0.36                                       | 47.38                                                               | 55.08                                            | 31.95                                               | 17.45                                                            | -                                  | 3.51                                 |
| R Fe                                                                     | 0.77                                                  | 99.29                                      | 23.12                                                               | 5.25                                             | 48.25                                               | 7.61                                                             | -                                  | 0.23                                 |
| R Na                                                                     | 26.90                                                 | 0.09                                       | 2.37                                                                | 1.25                                             | 0.63                                                | 0.00                                                             | -                                  | 46.62                                |

Table 1. – Chemical composition of the Givetian microspherules from the Givet area (quantifications in % of oxides). Values are an average of the total number of measurements; the minima and maxima values are indicated in brackets. <LD: below limit detection. Bold values highlight the main chemical components for each sample type. Calculation of the ratios R Al, R Fe and R Na is based on the glass components content except the silica (see Marini & Casier, 1997), as:  $R X = [(glass\ component\ X / sum\ of\ all\ the\ glass\ components) \times 100]$ . \* Glass-like carbon elements are composed of 80 to 85% of carbon (value obtained under ESEM, as undetectable under electronic microprobe because of carbon coating of the samples).

Tableau 1. — Compositions chimiques des microsphères givétiennes de la région de Givet (quantifications en % d'oxydes). Les valeurs indiquées sont une moyenne du nombre total de mesures ; les valeurs minimales et maximales observées étant indiquées entre parenthèses. <LD : sous la limite de détection de l'appareil. Les valeurs en gras mettent en avant les principaux composants chimiques pour chaque type d'échantillon. Le calcul des ratios R Al, R Fe et R Na sont basés sur la concentration en composants chimiques du verre, la silice exceptée (voir Marini & Casier, 1997), tel que :  $R X = [(composant\ du\ verre\ X / somme\ de\ tous\ les\ composants\ du\ verre) \times 100]$ . \* Les éléments de carbone vitrifié sont composés de 80 à 85% de carbone (valeur obtenue au MEB car indétectable à la microsonde électronique en raison de la métallisation au carbone des échantillons).

beds 1051 and 1052 (samples 161-st in Fig. 2A, B). Only these 6 samples with microspherules and glass-like carbon; 100 microspherules were retrieved from about 200 g of rock. In the Cul d'Houille section, on 11 samples from beds 34 to 37, 2 come from a dark clayey seal between beds 36 and 37. Only these 2 samples provided microspherules and glass-like carbon; 6 microspherules were retrieved from about 40 g of rock. For both sections, among the 106 microspherules found in this third level, 101 exhibit a smooth and glassy surface, sometimes pitted. Their shape is frequently spherical to spheroid with small droplets protrusions; more rarely elongate or bispherical. Most

of them are colourless, transparent to almost transparent; some are coloured and translucent (1 light-yellow, 1 black, 3 slightly red, 5 brown). The other 5 microspherules are opaque, dark grey and brightness with a crystallized surface (Fig. 3).

### 3) Analytical methods

Observations, pictures (Fig. 3), chemical quantifications (Table 1) and cartographies (Fig. 4) have been performed using an environmental scanning electron microscope Quanta 200 (ESEM), equipped with a backscattered electron detector

(BSE) and an energy-dispersive X-ray system (EDS or X-ray microprobe), and also using an Electronic microprobe Cameca SX 100. Before measurements, microspherules have been cleaned in chlorhydric acid in order to dissolve any gangue residues, then washed several times with tap water and dried. Analyzes and picturing have been performed on integral microspherules (ESEM), on thin sections (ESEM and microprobe) and on double-polished 100  $\mu\text{m}$ -thick sections (ESEM and microprobe). Chemical quantifications have been performed on 20 selected microspherules (at least one for each colour, see Table 1) and on some glass-like carbon elements from the three levels. For analyzes under electronic microprobe, the material has been carbon-coated. For picturing under ESEM, some material has been placed on stubs and gold-coated. The whole material is housed at the Catholic University of Lille (France) and figured material has been catalogued in the micropalaeontology collections of the Faculté de Gestion, Economie & Sciences of Lille (C.O.F.L.S. numbers, see Figs. 3 and 4).

#### IV. – CHEMICAL COMPOSITION AND STRUCTURE OF THE MICROSPHERULES

Quantifications of major and minor chemical elements are indicated in the Table 1. Chemical analyzes performed on the Fromelennes microspherules show six main chemical compositions, in relation with the colour of the microspherules. Type 1 includes the colourless and transparent spheres; they are rich in silica (~ 75%) and calcium (~10%). Type 2 includes the grey, opaque and brightness spheres; they are mainly composed of iron (more than 90%). Type 3 includes the red, yellow and light and dark brown translucent spheres; they are rich in silica (~ 60%), aluminium (~ 15%), iron (~ 8%), potassium (~ 3%), with sometimes slight variations in the proportions of these elements and also calcium (~ 3%) in some microspherules. Type 4 includes the black translucent spheres; they are rich in silica (~ 50%), aluminium (~25%) and calcium (~ 10%). Type 5 includes grey-brownish opaque spheres; they are rich in silica (~ 30%), iron (~ 30%), aluminium (~ 20%) and calcium (~ 6%). Type 6 includes colourless and transparent tubular microspherules; they are rich in calcium (~ 40%), silica (~ 35%), aluminium (~ 12%) and magnesium (~ 10%).

Iron-rich microspherules (type 2) show a crystallized dendritic surface (Fig. 3). Their content in iron is always over 90% (magnetite?) but there is no association with sulphur that allows to chemically distinguishing them from the small pyrite crystals that are abundant in the bed 1051 (Fig. 2B). All the other types (1, 3, 4, 5 and 6) show a glass matrix mainly composed of silica, but also of aluminium, potassium, iron, magnesium, calcium, sodium and titanium.

Chemical cartographies performed on thin sections of the material show two main internal structures:

- Homogeneous structures characterize the types 1 (Si-rich) and 2 (Fe-rich) of microspherules (Fig. 4). Internal vesicles have sometimes been observed. For the type 1, some microspherules show depletion in potassium, aluminium or calcium in their glass matrix.

- Heterogeneous structures characterize the other microspherules (types 3, 4, 5 and 6; Fig. 4). Numerous small crystallites are included within the glass matrix; they are mainly composed either of silica, or titanium and sulphur, or iron, phosphate and sulphur. Small vesicles are also frequently observed in the glass matrix. If silica is the dominant element, chemical composition of the glass matrix varies from one microspherule

to another. Chemical variations have also been observed within the glass matrix of some microspherules, with zones depleted or enriched in potassium, aluminium, calcium, titanium, or iron. A particular microspherule, spherical and brown under binocular lens, shows a large number of micrometre-sized crystallites mainly composed of iron, phosphate and sulphur, as well as numerous vesicles within a bi-phased glass matrix; the two phases of the glass matrix are chemically different (phase 1 in silica, iron, potassium, titanium and magnesium; phase 2 in silica, aluminium and calcium) and are radially alternated (Fig. 4).

Associated glass-like carbon elements are mainly composed of carbon (80 to 85 %), silica (~ 8 %), aluminium (~ 5%) and sulphur (~ 1.5 %). Micro-inclusions have been observed within these elements, of a mean-size of 5  $\mu\text{m}$  and rich in silica (~ 60%), aluminium (~ 35%) and potassium (~ 4%).

#### V. – DISCUSSION

Microspherules reported throughout the sedimentary record around the world can be broadly put in several categories, depending of their origin. When natural, they can have a biological origin (e.g. algae, conodont pearls...) or a mineral origin (e.g. impact glasses as microtektites, volcanic glasses, cosmic particles...). However, an artificial origin is also possible (silica man-made microbeads used for road reflective paintings, industrial residues, artificial glasses...).

##### 1) Invalidity of an artificial contamination

By care and as usual in numerous studies dealing with microspherules (e.g. Marini, 2003; Marini & Casier, 1997; Wang & Chatterton, 1993), it has been assessed whether such microspherules were artificial contaminants. In this way, some artificial microbeads used for road painting have also been chemically analyzed to compare (Table 1 and Fig. 5). However, several observations exclude the hypothesis of an artificial contamination for the Fromelennes microspherules:

Microspherules are present and abundant in three thin levels only within the 500 m-thick Givetian carbonate sequences of the Givet area (Fig. 2). Despite a bed-by-bed sampling, no microspherule or glass-like carbon element was found in another bed of the studied sections. In the three levels, several samples were taken in surface of the beds and also within the rock; all the samples provided microspherules and/or glass-like carbon elements.

The Fromelennes Fm. level has been found in two sections, the Flohimont and the Cul d'Houille sections. Both precisely correlated sections (Maillet *et al.*, 2013) are distant of about three hundred metres (Figs. 1 and 2) from each other.

The Fromelennes area is not an industrial area. Furthermore, if the Flohimont section extends along a road, beds of the Cul d'Houille section crop out along a small river.

The microspherules exhibit a large panel of shapes (spherical, ovoidal, tubular, tear-drop...), colours (colourless, yellow, brown, black, red, grey...) and aspects (smooth glassy surface, crystallized surface, pitted surface, protrusions, transparency, translucency, opacity...) (Fig. 3).

The microspherules show a large set of chemical compositions, with chemical heterogeneity observed in some microspherules, as well as the presence of internal vesicles and micro-inclusions chemically different from the glass matrix (Table 1 and Fig. 4).

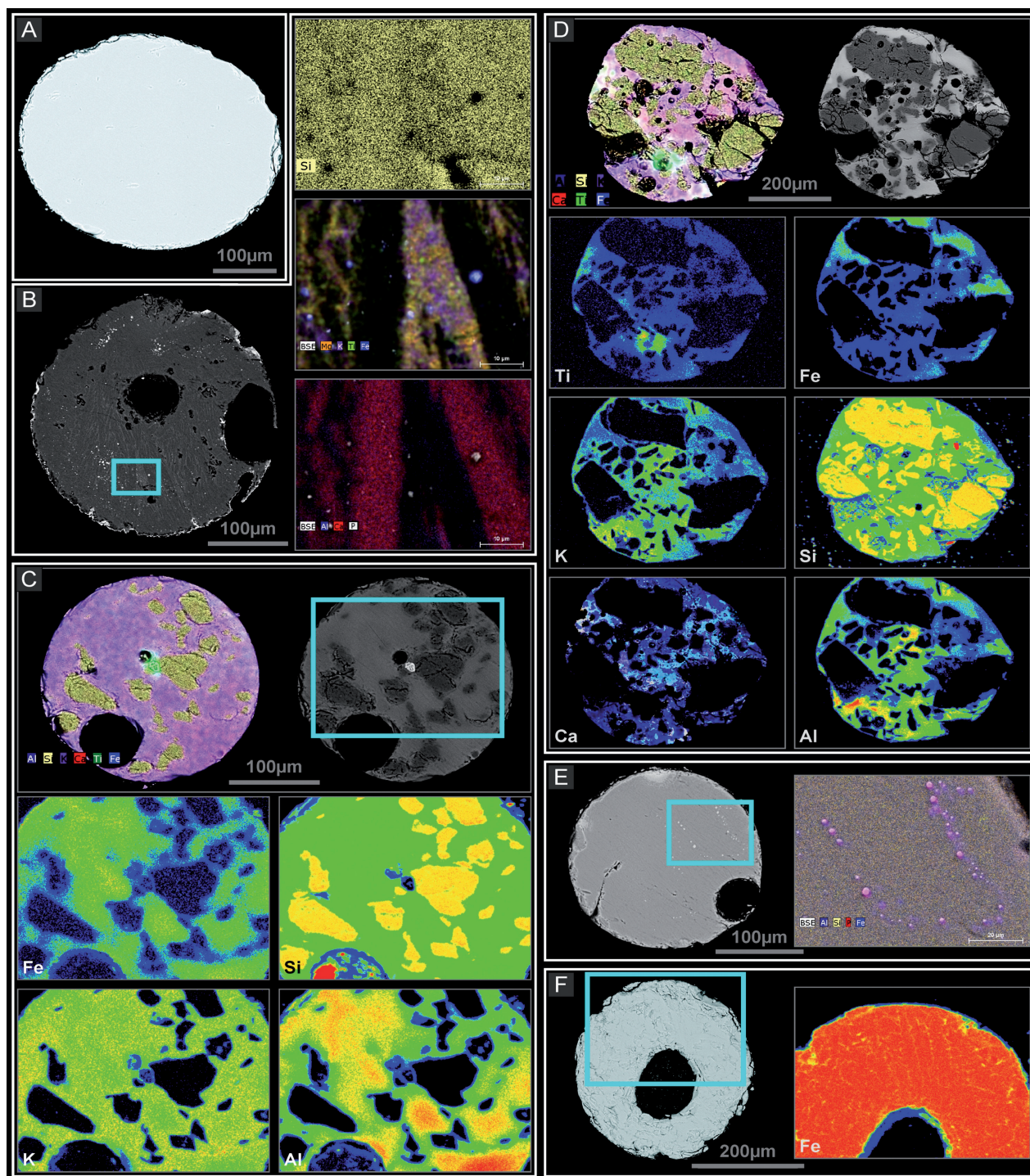


Fig. 4. – Micrographs and chemical cartographies of some thin sections of the Givet microspherules. A: Colourless transparent microspherule (type 1) with an homogeneous internal structure in silica (bed 1051, C.O.F.L.S. 1174); B: grey-brownish translucent microspherule (type 5) showing a glass-matrix with two chemical phases (Si-Al-Ca and Si-Mg-K-Ti-Fe) and micro-inclusions of iron phosphate (bed 718, C.O.F.L.S. 1175); C: Yellow translucent microspherule (type 3) showing crystallites (Si and Ti) and vesicles within a glass-matrix (bed 1051, C.O.F.L.S. 1176); D: dark brown translucent microspherule (type 3) showing crystallites (Si and Ti) and vesicles within a glass-matrix (bed 718, C.O.F.L.S. 1163); E: black translucent microspherule (type 4) showing a large vesicle and micro-inclusions of iron phosphate (bed 718, C.O.F.L.S. 1177); F: Grey, opaque and brightness microspherule (type 2) with an homogeneous internal structure in iron and a large central vesicle (bed 1051, C.O.F.L.S. 1170).

Fig. 4.— Clichés au MEB et cartographies chimiques de quelques sections polies des microsphérules de Givet. A : Microsphérule incolore et transparente (type 1) avec une structure interne en silice, homogène (banc 1051, C.O.F.L.S. 1174) ; B : Microsphérule gris-brunâtre et translucide (type 5) montrant une matrice vitreuse avec deux phases chimiques (Si-Al-Ca et Si-Mg-K-Ti-Fe) et des micro-inclusions de phosphate de fer (banc 718, C.O.F.L.S. 1175) ; C : Microsphérule jaune et translucide (type 3) montrant des cristallites (Si et Ti) et des vésicules au sein d'une matrice vitreuse (banc 1051, C.O.F.L.S. 1176) ; D : Microsphérule marron foncé et translucide (type 3) montrant des cristallites (Si et Ti) et des vésicules au sein d'une matrice vitreuse (banc 1051, C.O.F.L.S. 1163) ; E : Microsphérule noire et translucide (type 4) montrant une grande vésicule et des micro-inclusions de phosphate de fer (banc 718, C.O.F.L.S. 1177) ; F : Microsphérule grise, brillante et opaque (type 2) avec une structure interne homogène, en fer, et une grande vésicule centrale (banc 1051, C.O.F.L.S. 1170).

Glass-like carbon elements are always associated to the microspherules. They also exhibit internal silicified micro-inclusions (Figs. 3 and 4).

A major chemical difference is observed with industrial glasses: the latter are rich in sodium (7 to 15%; Fig. 5, see also Marini, 2003) and poor in aluminium (1 to 4%; *ibid.*), by contrast to the Fromelennes microspherules and to natural volcanic and impact glasses.

## 2) The Fromelennes microspherules: evidence for several punctual events during the Givetian

All previous observations support a natural origin of the Fromelennes microspherules and the associated glass-like carbon elements. Regarding their features (morphology, structures, inclusions, chemical composition...), the Fromelennes microspherules have obviously not a biotic, but well mineral origin. By their presence in only three precise levels within Givetian carbonate sequences, these microspherules seem to mark three punctual events. A first hypothesis is that the Fromelennes microspherules could be volcanic glasses. Indeed, some volcanoes were active during the Givetian on the Rheno-hercynian margin (Salamon & Königshof, 2010; Königshof *et al.*, 2010), of which the Ardenne massif belongs. Despite this, some observations do not seem to support the volcanic hypothesis:

The large panel of morphologies, structures and chemical compositions (Table 1, Figs. 3 and 4) of the microspherules within each level is unfavourable to eruptive phenomena, of which signatures in each level would be more singular and homogeneous.

The presence of ferrous microspherules (type 2) and glass-like carbon elements is not explained. About glass-like carbon elements, their general aspect (mm-sized, dark colour, spongy-aspect...; see Fig. 3) would remind volcanic ashes. However, these elements are exclusively chemically composed of carbon (70 to 85%), silica (6 to 15%) and aluminium (5%) (Tabl. 1), and show numerous internal micro-inclusions in silica and aluminium; all the other major chemical elements usually composing rhyolitic to basaltic tephra, such as sodium, calcium, iron and magnesium, are not found here.

All the Fromelennes microspherules exhibit geometrical shapes, of which most of them are perfect spheres (Fig. 3), on the contrary to volcanic residues (ashes, glasses...) which often are irregular. However, the few tubular glassy microspherules, found exclusively within the bed 718, may remind volcanic glass fibres like Pele's hairs.

The glassy microspherules from Fromelennes are abundant and very well preserved. Because of a high hydration, volcanic glasses would not be as well preserved in Devonian deposits (Claeys & Casier, 1994).

Another hypothesis is that the Fromelennes microspherules have an extraterrestrial origin. Indeed, following important asteroid impact, ejectas coming from melting and pulverization of the target terrestrial rocks are usually deposited on wide areas around the impact point. At distance at least larger than 10 times the crater diameter, such ejectas are mainly composed of submillimetre-sized glassy microspherules and are called distal ejectas (Glass & Simonson, 2013). Two main kinds of microspherules can be formed after an asteroid impact: microtektites and microkrystites (French & Koeberl, 2010). Microtektites result from the melting of terrestrial material while microkrystites are formed from the partial vaporization of the asteroid (Glass & Burns, 1988). According to the definition of Glass & Burns (1988), microtektites are characterized by a glassy aspect, a regular morphology

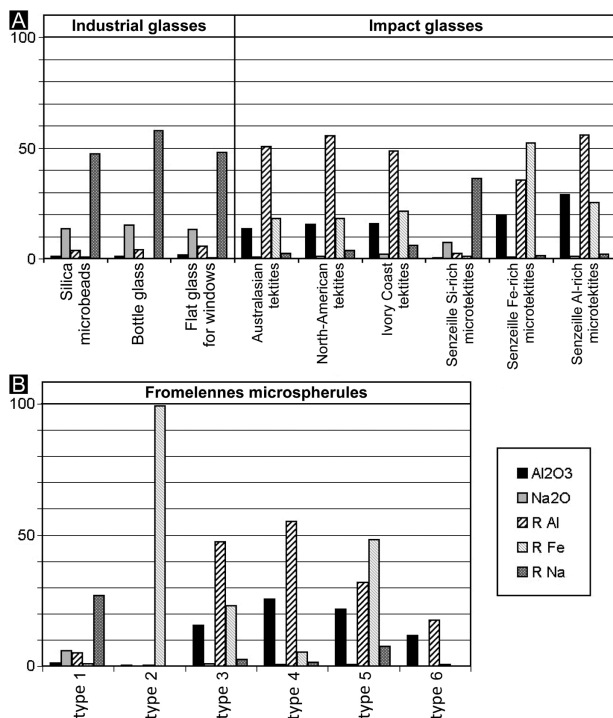


Fig. 5. – Comparison of several chemical ratios allowing to discriminate between various types of artificial glasses and impact glasses. See main text and caption of the table 1 for calculation of the ratios. A : data from Marini & Casier (1997); B : microspherules from the Givet area (this paper).

Fig. 5. – Comparaison de plusieurs ratios chimiques permettant de différencier divers types de verres artificiels et de verres d'impact. A : données de Marini & Casier (1997) ; B : microsphères de la région de Givet (cette étude).

(perfect sphere to tear-drop shape, with sometimes small droplets protrusions), a homogeneous structure, and the presence of lechatelierite (i.e. pure silica). They can present internal bubble-shaped cavities but contain no crystallites or remains of the original material. On the field, they are not necessarily associated to an iridium anomaly. They are usually larger (250 to 400  $\mu\text{m}$  of diameter) than microkrystites. Microkrystites, sometimes also named clinopyroxene-bearing spherules, are cosmic particles containing internal crystallites such as spinelle, clinopyroxene or sanidine (Glass & Burns, 1988; Glass *et al.*, 2004; Szöör *et al.*, 2001). By opposition to microtektites, microkrystites often exhibit a heterogeneous structure and never contain lechatelierite. They have an irregular spheroid shape, often a nickel core and are smaller than microtektites (150  $\mu\text{m}$  to 250  $\mu\text{m}$  of diameter). On the field, they are frequently associated to an iridium anomaly.

Regarding features of the Fromelennes microspherules, the glassy transparent colourless ones (type 1) may correspond to microtektites by their range of sizes, their richness in silica and their homogeneous structure with sometimes presence of internal vesicles. The other glassy microspherules (coloured spherical types 3, 4, 5 and tubular type 6) are more likely microkrystites by their smaller size and their heterogeneous structures and chemical compositions with numerous micro-inclusions. Grey and opaque ferrous microspherules (type 2) may be cosmic particles resulting from the partial vaporization of the meteor. Several observation and comparisons to the literature support that the Fromelennes microspherules may be evidence of several impacts during the Givetian:

By their large range of shapes with frequent small droplet protrusions, colours, chemical compositions and internal structures (Table 1, Figs. 3 and 4), the Fromelennes microspherules are very similar to the microtektites reported around the Frasnian/Famennian boundary in the Senzeille and Hony sections (Claeys & Casier, 1994; Claeys *et al.*, 1992; Marini & Casier, 1997). In particular, the Fromelennes microspherules of type 1 are chemically very close to the colourless transparent Si-rich microtektites from the Senzeille and Hony sections; the types 3 and 4 from Fromelennes are similar to the Al-rich microtektites from Senzeille and Hony sections; the type 5 from Fromelennes is comparable to the Fe-rich microtektites from Senzeille and Hony sections (Table 1).

The large range of chemical compositions with high contents in silica, aluminium and iron, is comparable to the ones usually known for distal ejectas. All the chemical elements (Si, Al, Fe, Ca, Mg, K and Na) encountered in the classical components of microtektites and microkrystites (e.g. sanidine, spinelle, clinopyroxene, silica-polymorphs, see Koeberl & Beran, 1988) are abundant in the Fromelennes microspherules.

On the contrary of artificial glasses, microtektites are characterized by high aluminium content and low sodium content (Marini & Casier, 1997). Except for the type 1, aluminium content of the Fromelennes microspherules is always far higher than the sodium content (Table 1 and Fig. 5); K<sub>2</sub>O/Na<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub>/(Na<sub>2</sub>O + K<sub>2</sub>O) ratios also show high values as usual in most of impact-glasses (Marini & Casier, 1997).

The Fromelennes microspherules exhibit an amorphous silica-rich glass-matrix (excepted for the iron spheres of type 2) and vesicles and/or internal crystallites are found within this matrix (Fig. 4). Some of these crystallites are silica-rich and show a high relief under polarized light. Fine analyzes of their chemical composition and the nature of chemical bonds indicated that it is pure silica: they might be silica-polymorphs as lechatelierite, coesite or stishovite.

The Fromelennes glass-like carbon elements are comparable to the abundant glass-like carbon reported in distal ejectas of the Younger Dryas impact (Firestone *et al.*, 2010). The formation of glass-like carbon requires high pressure and temperature; its origin might be due to pulverization during the impact of terrestrial carbonate rocks and/or to vitrification of organic matter particles.

### 3) Givetian microspherules elsewhere?

Impact microspherules are unusual deposits in sedimentary record, being both rare and punctual events in the geological time. However, because the microtektites are deposited on wide areas and usually globally around an impact crater, it might be possible to find them in Givetian rocks in other places. Around the world, several impact evidences have been reported in the Devonian, most of them in Upper Devonian deposits (e.g. Claeys *et al.*, 1992; Claeys & Casier, 1994; Masaitis, 2002; see also Maillet, 2013 for synthesis), but none to date is, to our knowledge, reported within the Givetian: only some microspherules have been found at the Eifelian/Givetian boundary in Morocco (Ellwood *et al.*, 2003; Schmitz *et al.*, 2006) and at the Givetian/Frasnian boundary in North-America (Isachsen, 1998). None of these levels correspond to the Fromelennes levels reported herein.

However, some authors reported the presence of 'egg cases' (Stauffer, 1940) in Givetian deposits: egg cases are known to be either conodont pearls if in fluoroapatite or impact spherules if siliceous (Stauffer, 1940; Wang & Chatterton, 1993). In the Boulonnais area (France), Magne (1964) reported abundant 'egg cases' in the 'term A' of the Griset Member (extreme base of the Blacourt Fm.), and figured one specimen (pl. XIII, fig. 56 in Magne, 1964). This level, to-day inaccessible, is of an early Givetian age: located below the base of the lower *P. varcus* conodont Zone and providing *Polygnathus ensensis* (see Brice, 1988), it could be assigned either to the *P. hemiansatus* Zone or to the lower lower *P. varcus* (*Polygnathus timorensis*) Zone in the standard conodont biozonation. Moreover, this egg case level is overlain by evaporitic and mudcrack levels (Mansy *et al.*, 2007) and by beds providing large-sized Leperditiid ostracods (Lethiers, pers. comm.); i.e. by sequences analogous to the upper part of the Trois-Fontaines Fm. in the Ardenne (Boulvain *et al.*, 2009; Maillet, 2013). Thus, the egg case level of Magne (1964) could correspond in the Fromelennes area to the Trois-Fontaines Fm. microspherules level (= bed 650 herein). In the Saoura area (Algeria), Le Fèvre (1963) reported abundant 'egg cases' into a carbonate unit of the Chefâr el Ahmar Fm. in the Km 30 section. This level belongs with doubt to the lower lower *P. varcus* Zone (Paris *et al.*, 1997; Maillet *et al.*, 2012) and possibly corresponds in the Fromelennes area to the Terres d'Haus Fm. microspherules level (= bed 718 herein).

### 4) What about impact structures in the Givetian?

Beyond microspherules, no impact crater dated of a Givetian age has been reported around the world. However, a synthesis of impact structures reported in the Devonian (see Maillet, 2013) added to chronostratigraphic and palaeogeographical considerations show that at least five imprecisely dated impact craters might be contemporaneous of the Fromelennes levels: (1) La Moinerie (Canada, 400 +/- 50 Ma, 8 kms of diameter); (2) Nicholson (Canada, < 400 Ma, 12.5 kms of diameter); (3) Brent (Canada, 396 +/- 20 Ma, 3.8 kms of diameter); (4) Elbow (Canada, 395 +/- 25 Ma, 8 kms of diameter) and (5) Kaluga (Russia, 380 +/- 5 Ma, 15 kms of diameter). To form and disperse distal ejectas on wide to global scales, the impact must be consequent: it means that diameter of the impact crater should be of a great-size, i.e. over about 10 km (Grieve, 1997). Therefore, the Brent crater appears to be too small and the Elbow crater appears to be too far during the Givetian to be adequate. Despite very rough dating, the La Moinerie and Nicholson craters are potential candidates regarding their sizes. Finally, the Kaluga crater is an excellent candidate, both by its size and its proximity to the Ardenne during the Givetian (Masaitis, 2002). However, it is also possible, on one hand, that none of these craters correspond to the Fromelennes levels and that other impact structures have to be discovered, or, on the other hand, that no trace of impact structures have been preserved (e.g. impact in deep-oceanic realm...).

## VI. – CONCLUSIONS

This is the first time around the world that glassy and ferrous microspherules, as well as glass-like carbon elements, are reported in Givetian deposits. Their natural origin is attested, but their formation remains questionable. If the volcanic origin

hypothesis cannot be definitively invalidated for some of them, many observations support that these microspherules may be distal ejectas (i.e. microtektites, microkrystites and cosmic particles) resulting of several asteroid impacts during the Givetian. To date, no impact evidence has been attested within the Givetian, however, an ‘egg case’ level reported by Magne (1964) in the Boulonnais area could be correlated to the level of the Trois-Fontaines Fm. and another ‘egg case’ level reported by Le Fèvre (1963) in the Saoura area might correspond to the level of the Terres d’Hauris Fm. Nonetheless, to validate the hypothesis of three distal ejectas levels within the Givetian carbonate sequences of the Fromelennes area, more data, more material and more analyses are necessary. Fundamental analyses on the microspherules are to confirm presence of high pressure/high temperature silica-polymorphs (as lechatelierite, stishovite or coesite) within the glass matrix by means of Raman spectroscopy and also to quantify the water content of the microspherules by means of Infrared spectroscopy (Koeberl & Beran, 1988). However, since microspherules alone are often not diagnostic to attest of an asteroid impact (French & Koeberl, 2010), it is essential to avoid any misinterpretation to look for additional impact-evidences, such as heavy elements (iridium, osmium, platinum...) or traces of shock-metamorphism (shocked quartz, nanodiamonds...) within the Fromelennes levels or in contemporaneous deposits in other places. Whether volcanic episodes or impact evidences, the three levels reported

herein consequently correspond to singular and instantaneous deposits on wide area (even global); thus, they could be excellent chronostratigraphic tools useful for wide-scale correlations. Although very tenuous, it should be possible to find these levels in many other places in the Ardenne and in farther areas, and thus use them to refine palaeogeographical models. Finally, another question to solve would be the consequences of such events on the Givetian living communities and their possible relationships with the Givetian bioevents leading to the end-Devonian mass extinction.

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