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Definition, classification and microfacies characteristics of oolitic ironstones used in the manufacturing of red ochre
A comparative petrographical analysis of Palaeozoic samples from France, Belgium and Germany

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Abstract

A brief overview is given of the classification schemes and current terminology of Phanerozoic sedimentary iron deposits, particularly that of ironstones. Representative geological samples of oolitic ironstones (OIS) possibly used as raw materials for prehistoric red ochres have been petrographically investigated. Microfacies differences have been observed between Llanvirn OIS from Normandy (France), Famennian OIS from Belgium and Emsian-Eifelian OIS from the Eifel area (Germany). Petrographical differentiation is based upon contrasting grain size, mineralogy and typology of the ferruginous ooids, as well as differences in mineralogy, diagenetic history and lithologic nature of the host sediments or of the cement. Most conspicuous are the differences in ferruginous ooid typology, including "true" concentric ooids, superficial ooids, algal oncoids and pseudo-ooids (such as ferruginized cortoids and rounded bioclasts). "Flaxseed ore" facies and "fossil ore" facies can be identified, as well as transitional or mixed types. A selection of representative archeological objects (OIS) has been petrographically investigated as well: the first results point to a rather local provenance for the samples of Normandy and Hesbaye (Belgium).

Keywords: Oolitic ironstone, petrography, ooids, Prehistory, fossil ore, flaxseed ore, Belgium, France, Germany.

Résumé

Un bref résumé de la classification et de la terminologie moderne des dépôts de fer phanérozoïque est présenté et plus spécialement celle des minerais de fer. Des échantillons géologiques représentatifs des minerais de fer oolithiques (OIS), susceptibles d'avoir été utilisés comme matière première pour la fabrication d'ocre rouge durant la préhistoire, ont fait l'objet d'une étude pétrographique. Des différences de microfaciès ont été mises en évidence entre les OIS d'âge Llanvirnien de Normandie (France), les OIS du Famennien de Belgique et les OIS d'âge Emsien-Eifelien de l'Eifel (Allemagne). La différenciation pétrographique se base sur les contrastes de tailles de grains, l'assemblage minéralogique et la typologie des ooïdes ferrifères ainsi que des différences de minéralogie, d'histoire diagénétique et de nature lithologique du sédiment hôte ou du ciment. Les différences les plus visibles se trouvent dans la typologie des ooïdes ferrugineux tels que les ooïdes « vraies » à structure concentrique, les ooïdes superficielles, les oncoïdes d'origine algaire et les pseudo-ooïdes (cortoïdes et les bioclastes roulés ferruginisés). Deux faciès peuvent être identifiés : "Flaxseed ore" (minerai dont les ooïdes sont en forme de graines de lin) et "fossil ore" (minerai riche en fragments de fossiles), ainsi que des faciès mixtes ou intermédiaires. Une sélection d'artéfacts représentatifs (OIS) a été investiguée pétrographiquement dont les premiers résultats démontrent une provenance locale pour le matériel archéologique de Normandie et de Hesbaye.

Mots-clés *: Minerai de fer oolithique, pétrographie, ooides, Préhistoire, minerai fossilifère, minerai de type « graine de lin », Belgique, France, Allemagne.*

1 INTRODUCTION – IRON FORMATIONS AND IRONSTONES

Iron occurs worldwide in most sedimentary rocks at a concentration of a few percent, but less commonly it is concentrated and forms so-called *ironstones* or *iron-formations*, with an iron content exceeding 15 %. In general, the behavior of iron and the precipitation of iron-rich minerals (oxides, carbonates, silicates and sulfides) are strongly controlled by the ambient chemistry and by diagenetic environments. Iron formation is the sedimentary product of a complex interplay among mantle, tectonic, oceanic and biospheric processes. Although many aspects of their origin still remain unresolved, it is widely accepted that secular changes in the style of their deposition are linked to the environmental and geochemical evolution of the earth (Bekker *et al.*, 2010). The majority of these sedimentary iron deposits were formed under shallow marine conditions and many of the Phanerozic examples contain marine fossils. However, there are important differences between sedimentary iron deposits that formed in the Precambrian and those of the Phanerozoic. The first group, well known as *iron-formations* or *banded iron formations (BIF's)* consists of thick units of thinly bedded or finely laminated chemical/biochemical sediments. They are composed of various iron-bearing minerals (mostly hematite or magnetite) interbedded with chert (jasper), deposited in large intra-cratonic Proterozoic (Precambrian) sedimentary basins. Geochronological studies emphasize the episodic nature of the deposition of the latter giant iron formations, as they are coeval with, and genetically linked to, time periods when large igneous provinces were emplaced (Bekker *et al.*, 2010). The second group, the post-Precambrian granular iron formations (GIF's) or Phanerozic ironstones are rather thin units, often lenticular and commonly displaying an oolitic aspect. They were deposited in localized areas of shallow-marine shelf settings: these are the *oolitic ironstones (OIS)*. The latter were already mined as an iron ore in Roman times and were a key resource in the industrial revolution of Western Europe (Tucker, 2001; Young, 1993; Evans, 1980).

A puzzling factor for the interpretation of many OIS is that there are no good modern analogues for comparison. Important aspects that are still matters of speculation are the exact sources of iron, the means of transport and the exact formation mechanisms of the OIS (Young & Taylor, 1989).

Finely ground OIS were used as a source of deep red pigments (called red ochre) in prehistoric times. Red ochre has been widely used for ceremonial, mortuary and other purposes, at least since Middle Paleolithic times and particularly during the Linear Pottery Culture (Linearbandkeramik - LBK) (Hamon, 2011; Jadin, 2003).

In this paper we will focus on the microfacies (microscopical) characteristics of the Paleozoic OIS that have been used for the manufacturing of red ochre (Billard *et al.*, 2012). Furthermore, a petrographical comparative analysis has been carried out on representative samples of OIS from the Llanvirn (Middle Ordovician) of the Basse Normandie (France), the Famennian (latest Upper Devonian) of the Ardennes (Belgium) and the latest Emsian of the Eifel area (Germany). More details regarding these particular stratigraphic levels and their geological setting are given in Goemaere *et al.* (2016: this volume).

2 PHANEROZOIC SEDIMENTARY IRON ORES – CLASSIFICATION AND TERMINOLOGY

Phanerozic sedimentary iron ores are widespread and all classes of deposits have been exploited from the Iron Age to the present. In order of increasing economic importance, the main classes are bog iron ores, clay ironstones and oolitic ironstones (OIS), including minette-type ores and Clinton-type ores. Only the last two have been industrially mined. Oolitic ironstones were exploited from approximately 500 deposits worldwide, with declining world importance because of the competition from the huge reserves of Precambrian banded-iron formations (BIF's).

Bog iron ore (*limonite des marais*; *Sumpferze* or *Wiesenerze*; *moerasijzererts*) consists of hydrated iron oxide minerals such as limonite and goethite, all formed by precipitation of iron-rich groundwater flowing into wetlands. The iron content varies from 50 to 30 % or less. Bacterial activity especially contributes to formation of the ore. Bog iron ore is often associated with peat deposits. Economically useful deposits can regrow within 20 years after harvesting. Bog iron was widely used as a source of iron in the past. This iron ore was discovered during the pre-Roman Iron Age and most Viking-era iron was melted from this ore. Bog iron ore has a brown to black color, often a sponge-like texture and a metallic luster (Denayer *et al.*, 2011). Bog iron ore has also commonly been used as a building stone, e.g. in the Low Countries (Belgium and The Netherlands) and the UK.

Clay-ironstone (*carbonate de fer du Houiller*; *Toneisenstein - Kohleneisenstein*; *sideri-etknollen*) is a mixture of clay and siderite (iron carbonate) or sphaerosiderite (globular micro-concretions of siderite) that sometimes occur as sheets or layers of dark-grey to brown, fine-grained nodules, both overlying or underlying coal seams. It is an impure carbonate of iron, containing generally from 30 to 35 % of metallic iron mixed with varying proportions of clay, oxide of manganese and lime. When coal is present the variety thus formed has a black colour and is therefore called "blackband". The enclosing sediments clearly show that they were deposited in environments intermediate between delta top alluvial floodplains and coastal plain swamps. The blackbands are therefore considered as fossil bog iron ores, formed in a similar way as recent bog iron ores (Boardman, 1989). They were discovered in the earliest 19th century in Scotland and used as an iron ore since 1930 in the UK and in Germany.

"Oolitic ironstones" *(OIS)* (*oolithes ferrugineuses*; *Eisen Rogensteine - Roteisenoolithe*; *oolietisch ijzererts*) occur as thin, often lenticular beds interlayered within shallow-marine and transitional (intertidal) carbonates, mudrocks or shales, and sandstones. The ore units generally show thicknesses a few tens of decimeters to a few tens of meters at the most, but display lateral extensions up to 150 km. Furthermore, OIS are frequently associated with rich fossiliferous and condensed deposits. OIS generally display an oolitic texture: they are composed of small ferruginous spherical or concretionary grains formed by thin concentric layers, called ooids (or ooliths, see further). Sedimentary structures such as cross-bedding, ripple marks and small scour and fill channels are abundant, testifying to the deposition in high-energy environments. The ooids themselves are formed during sea level lowstands or in condensed sections (Teyssen, 1989). Maynard and Van Houten (1992) suggested that OIS were deposited during still-stand following the peak of regression and prior to the peak of transgression. Some sedimentological features indicate storm-generated characteristics pointing to storm beds or tempestites (Dreesen, 1982; 1989; Cotter & Link, 1993). The exact origin of the ferruginous ooids and the provenance of the iron, however, remain still debatable (Young & Taylor, 1989). Different models or mechanisms have been proposed: primary abiogenic precipitation of iron minerals versus replacement of calcareous ooids or even microbially triggered deposits; land-derived origin of the iron (e.g. diagenetic alteration of lateritic soils) versus weathering of volcanic ashfalls or hydrothermal enrichment of sea water (Kearsley, 1989; Kimberley, 1979; Dahanayake & Krumbein, 1986; Préat *et al.*, 2000; Siehl & Thein, 1989; Van Houten & Bhattacharyya, 1982; Dreesen, 1989; Sturesson, 1992; Sturesson *et al.*, 2000; Laenen *et al.*, 2002).

Based on their general mineralogy, two classes of oolitic ironstones are distinguished: "Minette-type OIS"and "Clinton-type OIS" (Evans, 1993).

"Minette-type" *OIS* are the most common and most widespread OIS worldwide. They have an iron content of about 30-35 % by weight. These ironstones are found in shallow marine to intertidal carbonaceous shale, mudstone, marl, and limestone sequences. The dominant iron-bearing minerals are iron (3+) oxide-hydroxides (limonite), siderite and chamosite, with lesser amounts of other minerals (magnetite, hematite, greenalite and pyrite). Typically, the iron ores comprise ooids of alternating chamosite and limonite that have nucleated around detrital grains or fossil fragments. Minette-type OIS of Jurassic age have been mined as an iron ore in Europe during the nineteenth and twentieth centuries. Good examples include the East Midlands (Cleveland) ironstones (UK), the Minette-ores of Lorraine and Luxemburg and the Salzgitter ores of Saxony (Germany). Most Minette-type OIS appear to have originated through erosion and re-deposition of soil-derived ooids (lateritic soils) within shallow-marine to deltaic settings (Siehl & Thein, 1989). However, geochemical evidence (rare earth elements) rather suggests that synsedimentary volcanism was the probable source of the iron in minette-type Aalenian-Bajocian OIS from the Iberian Basin in Spain (Garcia-Frank *et al.*, 2012). Also, the absence of contemporaneous soil deposits and the lack of evidence of subaerial exposure in an arid paleoclimatic setting, rule out weathering processes as the main source of iron.

"Clinton-type OIS": this class of OIS is named after the Silurian Clinton Formation of the eastern United States of America (Cotter & Link, 1993): here, oolitic ironstones occur together with argillaceous and carbonaceous shales, limestones and dolostones, within shallow marine environments. They form deep-red to purple, massive to lenticular beds of hematitic-chamosite-siderite rock. The iron content is about 40-50 %. *Hematite*, chamosite and siderite are the main iron-bearing minerals and they are associated with calcite and silica. Hematitic OIS are also known as "oligiste oolithique" (FR) or "Roteisenerz" and "Rötel" (DE). They are common in rocks of Cambrian to Devonian age in eastern North America, Western Europe and Northern Africa. Classical Clinton-type OIS deposits include the Ordovician Wabana Formation of Newfoundland (Canada) and the Silurian Clinton Group of the central and southern Appalachians (USA). West-European examples are known from the Ordovician of Normandy and Bretagne (France), the Upper Devonian of the Ardennes (Belgium) and the Lower Devonian of the Eifel area (Germany). An extensive North African Paleozoic oolitic ironstone belt (over 3000 km long) can be followed from Mauritania, through Morocco, Algeria and Lybia: the belt encloses several OIS deposits within Silurian to Devonian formations containing over 10000 million tons of ironstone reserves (Guerrak, 1989).

According to the shape and the nature of the ferruginous components, Clinton-type OIS can be further subdivided into so-called "flaxseed ores" and "fossil ores". The former are OIS composed of concentrations of disk-shaped ooids that have been partially flattened parallel to the bedding plane. The shape of the flattened ooids resembles that of a flaxseed (*graine de lin*; *Leinsamen*; *lijnzaad*). Fossil ores are predominantly composed of skeletal fragments (bioclasts or fossil debris) that are either replaced by, or impregnated and coated with, iron-bearing minerals.

3 MICROFACIES CHARACTERISTICS OF CLINTON-TYPE OIS

The type deposits for Clinton-type OIS, the mid-Silurian Clinton-ores, consist largely of skeletal grainstone storm beds whose components (mainly skeletal fragments) are extensively impregnated and replaced by ferric oxides (Alling, 1947; Moorehouse, 1959; Cotter & Link, 1993). Other forms of iron mineralisation consist of ferruginized ooids and superficial ooids. Alling (1947) favoured the idea of a "diagenetic replacement": in his opinion, the "fossil" ores were the result of the partial replacement of the carbonate of the fossils and of the subsequent carbonate oolitic coatings. Because of the strong analogy of Clinton-type OIS with limestones, the classification of carbonates (e.g. Dunham, 1962) and the principles of carbonate microfacies analysis (e.g. Flügel, 1982) can be applied to the microfacies description of OIS, as previously suggested by T. Young (1993).

Microfacies is regarded as the total of all sedimentological and paleontological characteristics that can be described and classified from thin sections and other sample preparation types (e.g. acetate peels, polished slabs) or rock samples. During the past decades, microfacies analysis has become an established part of the study of carbonate rocks. Moreover, applied microfacies has become increasingly important in economic geology, including the study of oil and gas reservoirs, and that of raw materials, such as natural stones and sedimentary iron ores. Petrographical analysis by means of thin sections (*lames minces*, *Dünnschliffe*, *slijpplaatjes* [NL]) has become an important tool for tracing the provenance of historical building stones and archeological materials. In this paper we have applied microfacies analysis in order to differentiate between the microscopical textures of macroscopically analogous OIS deposits and to support evidence from more sophisticated geochemical investigation tools (such as XRF, HH-XRF and LA-ICPMS, see other papers in this book).

In OIS several components (grain types) can be identified, next to a fine-crystalline groundmass (the matrix), coarse-crystalline binding agents (the cement) and empty pore spaces (the porosity). Matrix (a detrital matrix of clay, mud or lime mud with a grain size generally <63 microns) will be present depending on the energy of the depositional environment. In high-energy environments the mud fraction will be winnowed away and a "clean" or lean sand-sized sediment will remain. Cements (e.g. calcite, dolomite, silica, iron-oxides, iron-silicates) are chemically precipitated in crystalline form from intergranular solutions and will fill up the original pore spaces.

3.1 Grain types in OIS

The following grain types can be easily identified in thin section (see Fig. 1) or with the hand lens (see also pictures in the paper by Billard *et al.*, 2016: this volume): non-skeletal grains and skeletal grains. Skeletal grains obviously are fragments of fossils (bioclasts) that were originally composed of calcite, magnesian calcite, aragonite or opaline silica. Non-skeletal components are defined as grains that do not appear to have been deposited as skeletal material: they include detrital grains (e.g. sand grains), coated grains, lithoclasts and intraclasts.

Detrital grains

Detrital grains in OIS are mostly composed of silt- (<63 microns) and sand-sized grains (<2 mm) that survived weathering and were transported to the depositional site as clasts. Their mineralogy generally corresponds to that of the enclosing or enveloping sediments (mudstones, siltstones, sandstones or limestones). They generally consist of angular to rounded grains of quartz and other common silicate minerals (e.g. feldspars, micas) or small rock (lithic) fragments.

"Lithoclasts" (or "extraclasts") (*lithoclasts*; *Lithoklasten*; *lithoklasten*)

These are irregular and somewhat larger fragments of rock that have been eroded and transported outside of the primary sedimentary basin to be deposited in another paleo-environment. The clast boundary cuts across cement and particles, reflecting its well-indurated nature. Lithoclasts are indicative of high-energy processes that rip-up, abrade and transport pieces of previously indurated rocks, such as fragments of limestone, mudstone, siltstone and sandstone. In our material, lithoclasts of ferruginized sandstone have been frequently observed, e.g. in the Lower-Middle Devonian OIS from the Eifel area.

Intraclasts (*intraclastes*; *Intraklaste*; *intraklasten*)

These grains consist of slightly indurated irregular fragments of the same rock type that were eroded and transported within the same sedimentary basin. Examples include carbonate mud lumps that are torn up from the bottom of lagoons during storms, hardened desiccated carbonate mud flakes produced in intertidal and supratidal environments and fragments broken from cemented crusts. Intraclasts also include aggregates of coated grains, including so-called grapestones or botryoidal grains. In our studied material, ferruginized intraclasts are quite common: they often comprise aggregates of ferruginized coated grains, e.g. in the Famennian OIS of the Ardennes (Belgium).

Coated grains (*grains revêtus*; *Rindenkörner*; *gelaagde korrels*)

Coated grains have a more or less well-defined nucleus, surrounded by a coating or by multiple coatings of carbonates, usually fairly fine-grained calcite, called the cortex. In many coated grains, this cortex is at least partially laminated. Since coated grains of similar appearance can form in different environments, a simple descriptive classification will be used here, following the usage of Tucker & Wright (1990). Coated grains include ooids, pisoids and oncoids. In OIS the coatings of the ferruginous coated grains, consist of iron minerals (replacement or primary precipitations) including berthierine (serptentine group member, formula: $[(Fe^{2+},Fe^{3+},Al,Mg)_{2-3}(Si,Al)_2O_5(OH)_4]$, chamosite [member of the chlorite group of general formula: $(Fe^{2+},Mg,Fe^{3+})_5Al(Si_3Al)O_{10}(OH,O)_8$], goethite [FeO(OH)] or hematite (γ-Fe_2O_3).

Ooids (*oolithes*; *Oolithe*; *oolieten* or *ooïden*) and pisoids (*pisolithes*; *Pisolithe*; *pisolieten* or *pisoïden*) are spherical to ellipsoidal, coated grains with a nucleus surrounded by a cortex of which at least the outer part is smoothly and concentrically laminated. Both terms are commonly used in the literature, although "ooid" is used for the particle and "oolith" for the rock composed of ooids. A rock composed of ooids has also an oolitic texture. Ooids are <2 mm in diameter, pisoids are >2 mm. They originate in shallow agitated waters with high saturation in calcite. The Great Bahama bank platform (Florida, USA) is a good modern analogue for Palaeozoic or Mesozoic depositional settings of calcareous ooids. Oncoids (*oncolithes*; *Oncolithe*; "*oncoïden*" or *oncolieten*) are coated grains in which the calcareous cortex is less smoothly laminated, with irregular laminae that are overlapping and that are often not entirely concentric. Oncoids are mostly very irregular in shape. They may have a poorly defined nucleus and may contain biogenic structures. Oncoids are larger than ooids (>2 mm). Micro-oncoids are defined as oncoids with a grain size < 2mm that can easily be mistaken for ooids. The latter however lack biogenic microstructures (e.g. encrusting algae or foraminifera).

Ooids display a variety of cortical structures and mineralogies, depending on their geological age, mode of formation and diagenetic history. Radial ooids and tangential ooids are distinguished on the base of their fabric or microstructure. However, the latter microstructure is often altered into fine-grained micritic calcite, most probably due to microbial activity (micritisation). Ooids with only one or two concentric layers are known as "superficial ooids". The nuclei generally consist of detrital grains (e.g. quartz grains in the sand fraction), limestone clasts or bioclasts. The nucleus of "multiple ooids" or "composite ooids" consists of several ooids. Furthermore, larger aggregates combining several ooids and/or multiple ooids, form complex coated grains, called "grapestones", "lumps" or "botryoidal grains". The term "Bahamite" has also been employed for designating the latter grain aggregates referring to their current area of formation, the Great Bahama Bank platform (Florida, USA).

Ferruginous ooids or ferruginized ooids are the real hallmark of OIS and different ooid types do occur: normal, superficial and composite ooids. Ooid typology helps to differentiate the different OIS (see further). Furthermore, due to burial and/or compression, some ooids tend to be somewhat squeezed parallel to the bedding plane, resulting in flattened ooids. In the case of OIS such flattened ferruginous or ferruginized ooids are commonly called "flaxseed iron ore".

"Pisoids" are smoothly laminated grains that are larger than 2 mm in diameter. They are much less common than ooids and form in specialized environments, such as lagoons, lakes, rivers and caves (the latter are also called "cave pearls"). In contrast with micro-oncoids they do not show good evidence for a biogenic origin (see further).

For the correct interpretation of any coated grain, it is essential to note the associated features in the host sediment, for ooids and pisoids themselves are not diagnostic or even characteristic of any particular environment.

Another particular class of ooids is that of the so-called *pseudo-ooids*: these are grains that strongly resemble ooids but lack the characteristic laminae. They include well-rounded skeletal grains (rounded bioclasts) and so-called cortoids. "Cortoids" belong to a specific category of bioclasts, ooids or lithoclasts, whose periphery shows a circumgranular, non-laminated micritic rim or a "micrite envelope" (mostly appearing as a dark rim in thin section). The latter envelope originates through micritisation (due to the effects of boring organisms and bacteria), a process whereby the margins of the carbonate grain (often a fossil fragment) or the total volume of the grain, are replaced by crypto- to microcrystalline carbonate (micrite). Ferruginized cortoids frequently occur in our studied material, e.g. in the Devonian OIS of Belgium and Germany.

"Oncoids" ("oncoliths") are mm- to cm-sized, rounded or irregularly formed grains consisting of a layered cortex and a bioclastic or lithoclastic nucleus. The layers originate from encrusting sessile organisms (predominantly cal-

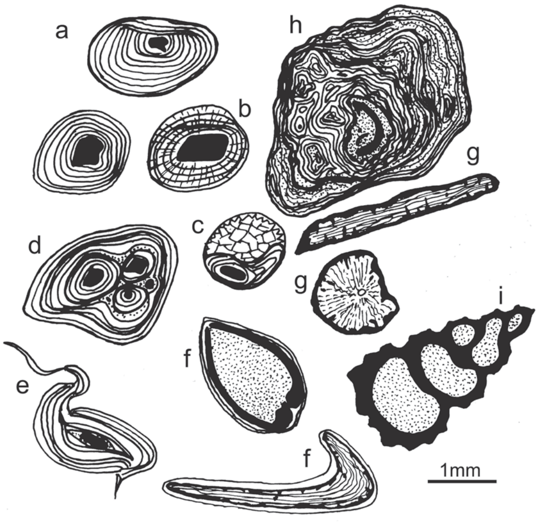

Fig. 1 – Typology of common skeletal and coated grains encountered in the OIS. All these grains can either be replaced by or impregnated and coated with iron minerals, producing ferruginous allochems. Ink drawings based on thin section micrographs (R. Dreesen). Legend: a : tangential ooid, b : radial ooid, c : collapsed ooid, d : composite (multiple) ooid, e : spastolith (deformed ooid), f : superficial ooid, g: cortoid (with micritic envelope), h: oncoid; i: bioclast (skeletal grain).

Fig. 1 – Typologie des grains du squelette et des grains revêtus rencontrés dans les OIS. Tous ces grains peuvent être remplacés ou imprégnés et revêtus par des minéraux ferrifères, produisant des allochèmes ferrugineux. Les dessins à l'encre sont basés sur les microphotographies (R. Dreesen). Légende : a : ooïde tangentielle, b : ooïde radiaire, c : ooïde collapsée, d : ooïde composite (multiple), e : spastolithe (ooïde déformée), f : ooïde superficielle, g : cortoïde (avec enveloppe micritique), h : oncoïde, i : bioclaste (grain du squelette).

cimicrobes and algae, but also other encrusting organisms such as foraminifera). Oncoids are common both in marine and non-marine environments. The organisms already mentioned above enhance and initiate the precipitation of calcite (in the case of limestones), act as encrusters and binders, trap fine-grained sediment or trigger synsedimentary lithification. Large ferruginized oncoids have been encountered in the Devonian OIS of both Belgium and the Eifel area.

"Skeletal grains" or *bioclasts* are fragments derived from microfossil shells or invertebrate skeletons (bioclasts or fossil debris). Calcitic-aragonitic bioclasts include skeletal fragments of calcareous algae, red algae, foraminifera, corals, stromatoporoids, calcareous sponges, echinoderms, brachiopods, bryozoans, trilobites, ostracodes... Skeletal grains of biogenic opaline silica (nominally $SiO_2.nH_2O$) mostly include sponge spicules and radiolarians. These bioclasts often tend to be abraded and rounded before being impregnated or coated with ferrous or ferric iron minerals. The high frequency of ferruginized bioclasts in several of our studied Famennian and Emsian OIS, allows us to identify "fossil ore" facies (see further).

"Particle deformation": coated grains, especially ooids, can be modified due to post-depositional collapse or deformation. Collapsed ooids underwent partial dissolution and internal collapse of the remaining undissolved material to the bottom of the mold. Furthermore, due to strong mechanical compaction, tectonic compression or shearing, ooids can be deformed showing distorted shapes and elephantine features, producing so-called "spastoliths", commonly with some separation of cortical layers from their nuclei. This kind of deformation clearly points to the softness of the original particles or the original composing minerals (e.g. chamosite). The latter deformed ooid-type has been encountered in our studied material, e.g. in the Ordovician OIS of Normandy and the Famennian OIS of Belgium.

3.2 Iron minerals in the OIS

"Hematite" is the most common iron mineral in Paleozoic OIS. In the latter it is mostly present as coated grains and as impregnations or replacement of fossils. Later diagenetic migration and replacement of the calcareous host sediment and of calcite cements by hematite is quite common. Although the hematite itself may be of primary origin (i.e. precipitated via a precursor such as an amorphous hydrated ferric oxide), there is often evidence that the oxide has formed by replacement of berthierine (Tucker, 2001). However, berthierine grains are often reworked into a more oxidizing environment where hematite is stable. In thin section hematite is opaque (deep brown to black) and cryptocrystalline. In reflected light, hematite can be recognized by its red color.

"Goethite" is a major constituent of OIS, especially of Mesozoic OIS such as the minette-type iron ores. Sometimes goethite appears to be a recent weathering product that resulted from the oxidation and hydration of other iron minerals. However, goethite appears also to be of primary or at least syn-sedimentary origin (Tucker, 2001). Goethite often forms perfectly spherical ooids, commonly consisting of alternating goethite and berthierine layers or cortices. The goethite could have formed through sea-floor oxidation of berthierine. In thin section, goethite is yellow to reddish brown in color and generally appears isotropic.

The most important green iron-rich silicate minerals in Phanerozoic OIS are *berthierine* and *chamosite*. In thin section it is quite difficult or even impossible to differentiate between them. A distinction is possible with the help of XRD-analysis. In thin section, berthierine and chamosite are both green in color and show a low birefringence. Berthierine is an iron-rich, layered silicate of the serpentine group, whereas chamosite is an iron-rich chlorite. Berthierine is the early diagenetic mineral, which will be soon transformed (by increasing temperature due to increasing overburden pressure) into chamosite. Most Jurassic minette-type OIS therefore contain berthierine, whereas the Paleozoic Clinton-type OIS contain chamosite. Berthierine and/or chamosite typically occur as ooids in Phanerozoic ironstones, within a cement of siderite or calcite. In many cases there are no nuclei to the ooids or they have formed around berthierine flakes or broken ooids. There is overwhelming evidence that they were soft at the time of compaction, because they are often flattened or distorted, displaying strange elephantine, trunk-to-tail textures (so-called spastoliths; Tucker, 2001).

"Magnetite" (Fe_3O_4) is only a minor component of Phanerozoic OIS. It generally occurs as small replacement crystals or granules within the OIS. It is distinguished from hematite by its steel-grey color in reflected light. Its very high magnetic susceptibility value is used to identify its presence, even at low concentrations.

"Siderite" ($FeCO_3$) is the cement of many Phanerozic berthierine/chamosite-rich OIS but it can also replace coated grains (ooids) and skeletal grains. In thin section siderite occurs as coarse crystals similar to other carbonates, in terms of high birefringence and rhomboedral cleavage. Siderite can be recognized by a yellowish brown oxidation zone along the crystal boundaries and by its rhombic cleavage planes. Ankerite and ferroan dolomite may be associated, but they are quite difficult to distinguish from siderite in thin section.

Iron sulphides, particularly *pyrite* (FeS_2), are common constituents of many iron-rich deposits including OIS. Pyrite is distinguished from other opaque iron minerals by its bright yellowish color in reflected light. It is present as disseminated grains and crystals and it often replaces skeletal fragments. Small grapelike aggregates of spherical micro-concretions of pyrite are known as framboids: these have been precipitated by sulphate-reducing bacteria, and are often associated with decaying organic matter.

OIS contain weathering-sensitive minerals like berthierine, chamosite, pyrite, and to a lesser extent, calcite, iron-rich dolomite and siderite (the latter being sensitive to dissolution). Fe^{2+} is oxidized into Fe^{3+} and will be precipitated with neo-formation of goethite or other iron mixtures (oxi-hydroxides) in outcrop. After heating, oxi-hydroxides can be transformed into a red hematite. This transformation can mask the primary sedimentary features.

3.3 Sedimentary structures

Sometimes the original depositional texture or stratification of OIS is disturbed by traces of burrowing organisms, called *bioturbations*. Common bioturbators are annelids and other infaunal or epifaunal organisms. These disturbances or bioturbations can be recognized in thin section by displaced sediment grains, abnormal alignments or completely disordered particles.

"Erosional unconformities" are interruptions or breaks in the sedimentation. They represent surfaces that separate older, eroded rocks from younger, overlying sediments. These unconformities may be related to transgression, carbonate dissolution, storm activity and clastic influx on carbonate shelves.

"Hardgrounds" are a particular type of bedding plane. They represent horizons of synsedimentary cementation that took place at or just below the sediment surface. A hardground is often encrusted by sessile organisms, pierced by boring organisms and often cuts across fossils and sedimentary structures. Hardground surfaces may become mineralized and impregnated with iron (hydr)oxides and other minerals (e.g. phosphates). Erosional unconformities and ferruginized hardgrounds have been frequently observed in Famennian OIS of Belgium (e.g. microstromatolitic hardgrounds. Hardgrounds mostly point to non-deposition events and condensed deposits, as proven by paleontological condensation within the Famennian OIS (Dreesen, 1989).

3.4 Petrographical nomenclature applied to OIS

A consistent classification and a correct concise naming of rocks are essential for effective communication. For the petrographical description of OIS we are applying the terminology used in the carbonate rocks classification, as previously proposed by T. Young (1989). Amongst the many classifications that have been introduced for carbonate rocks and sediments, only two - the Folk (1959/1962) and Dunham (1962) "textural classifications of limestone" - have successfully met the test of time. Embry & Klovan (1971) introduced some additional classes for describing reef, mud mound and other biogenic carbonates, whereas the Wright (1992) classification provided a balance in terminology between primary (sedimentologic-biologic) and secondary (diagenetic) features (Scholle & Ulmer-Scholle, 2003).

Sediment or sedimentary rock *texture* refers to the shape, size and three-dimensional arrangement of the particles that make up sediment or a sedimentary rock. Textures are primary, where the grains possess their arrangement that existed after they have been deposited (or after precipitation in the case of crystals). However, textures in sedimentary rocks are commonly secondary, because they have been altered by diagenesis or lithification in some way from their original condition. The most common diagenetic effect is that of compaction, where the weight of overlying sediments causes the components or grains to rearrange themselves, or even become deformed, fractured or dissolved. A fundamental approach in sedimentary petrography is the recognition of grain-supported versus matrix-supported textures. Grain-supported (*texture jointive*) is a term used to describe the texture in which large particles, such as clasts or coated grains within a matrix, are largely touching. Where grains are contained (or floating) in finer-grained matrix and are largely not in contact, the texture is described as matrix-supported (*texture empâtée*).

The following petrographical rock classes can be recognized on cut or polished surfaces (with a handlens) or in thin section. For OIS the suffix "ironstone" has been added to describe the appropriate rock types. It is essentially based on Dunham's limestone textural classification (see Tab. 1). In the petrographical terminology of OIS, the component (or allochem) mineralogy can be given before the component type and the groundmass mineralogy before the textural term (Young, 1989). Example: a matrix-supported ironstone with 15 % goethitic ooids in a berthierine-rich matrix should be named a "goethite ooidal berthierine wacke-ironstone".

4 MACROSCOPICAL AND MICROSCOPICAL CHARACTERISTICS OF PALEOZOIC OIS

Representative samples of Paleozoic OIS from the Llanvirn of Normandy (France), the Famennian of the Ardennes (Belgium) and the Emsian-Eifelian transitional beds of the Eifel area (Germany), that are suspected of having being used as raw material for archeological artefacts and red ochre manufacturing, have been petrographically studied in thin section. The preliminary results of this first comparative analysis of geological samples are listed in Table 2. Differences in typology of the ferruginous or ferruginized coated grains and varying mineralogy allow a first differentiation between the studied OIS.

Macroscopically, the deep red color and the oolitic texture of the OIS are most conspicuous in most studied geological samples. However, in the Ordovician OIS of Normandy, a dark greenish-grey oolitic facies occurs (the chlorite-carbonate facies) in addition to the regular red hematitic or oxide facies. At first glance, the Ordovician OIS tend to be more fine-grained, more homogenous and better sorted than the Famennian and Emsian-Eifelian OIS. The heterogeneity of the latter two OIS results from mixing of different types of ferruginous or ferruginized coated grains and other components. Fossiliferous limestone often represents the host sediment, such as in the Famennian OIS of Belgium and the Emsian-Eifelian OIS of the Eifel area. However, the host sediments of the Ordovician OIS are almost exclusively siliciclastic. The so-called flaxseed facies (containing compressed and flattened ooids) is prominent in both the Ordovician and the Famennian OIS, whereas the so-called fossil ore facies (composed of ferruginized or iron-coated bioclasts) are more characteristic of the Emsian-Eifelian and the Famennian OIS. On the other hand, the occurrence of micro-oncoids is quite characteristic for the Famennian OIS, whereas ferruginized oncoids, intraclasts and lithoclasts have been macroscopically identified in both the Famennian and Emsian-Eifelian OIS. Locally and occasionally, fer-

Matrix- supported		*Grain-supported*	
Grain size < 2 mm			
<10% grains Mud-ironstone	>10% grains Wacke-ironstone	With matrix Pack-ironstone	Without matrix Grain-ironstone
Grain size > 2 mm			
	Float-ironstone	Rud-ironstone	

Tab. 1 – Simplified textural classification scheme for OIS.
Tab. 1 – Classification texturale simplifiée des OIS.

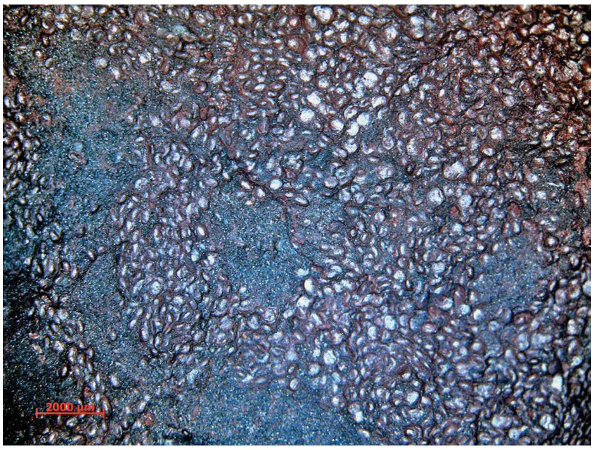

Fig. 2 – Ordovician OIS, Urville Shales Formation, May (Normandy, France). "Flax seed" ore facies: well-sorted, flattened hematitic ooids (oxide facies) in a chloritic-siliciclastic matrix. Macroscopical view of fresh rough surface. Scale bar is 2 mm.

Fig. 2 – OIS ordoviciennes, Formation des Schistes d'Urville, May (Normandie, France). Faciès du minerai en « graines de lin » : ooïdes (faciès oxydé) hématitiques plates et bien classées dans une matrice mixte chlorite-grains détritiques. Vue macroscopique d'une surface brute et fraiche. Barre d'échelle : 2 mm.

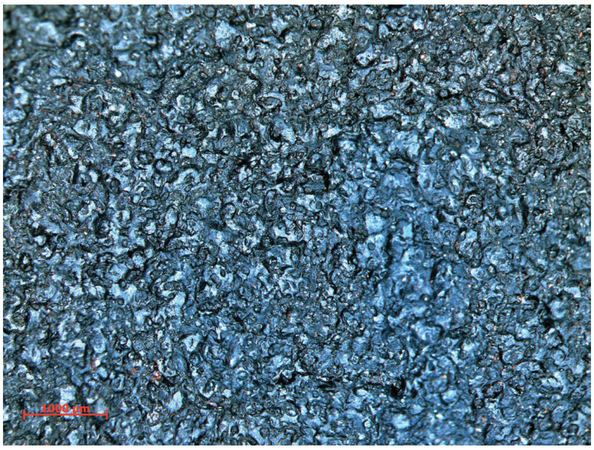

Fig. 3 – Ordovician OIS, Urville Shales Formation, May (Normandy, France). Dark greenish-grey chloritic facies with densely packed, slightly deformed and flattened small chloritic ooids. Macroscopical view of fresh rough surface. Scale bar is 2 mm.

Fig. 3 – OIS ordoviciennes, Formation des Schistes d'Urville, May (Normandie, France). Faciès chloritique gris vert sombre avec petites ooïdes chloriteuses plates et légèrement déformées en agrégat compact. Vue macroscopique d'une surface brute et fraiche. Barre d'échelle : 2 mm.

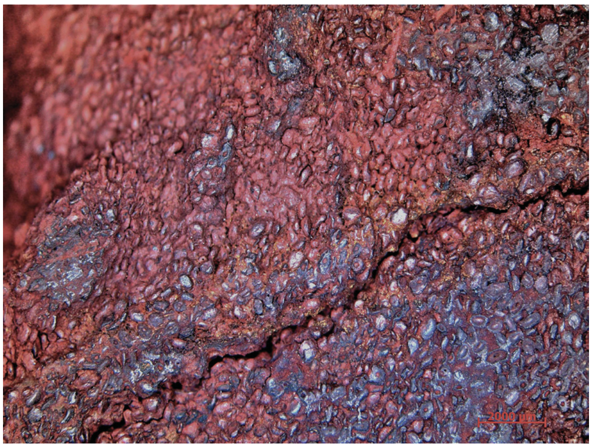

Fig. 4 – Ordovician OIS, Urville Shales Formation, Urville (Normandy, France). "Flax seed" ore facies. Weathered hematitic ooids. Macroscopical view of weathered surface. Scale bar is 2 mm.

Fig. 4 – OIS ordoviciennes, Formation des Schistes d'Urville, May (Normandie, France). Faciès du minerai en « graines de lin ». Ooïdes hématitiques altérées. Vue macroscopique d'une surface brute altérée. Barre d'échelle : 2 mm.

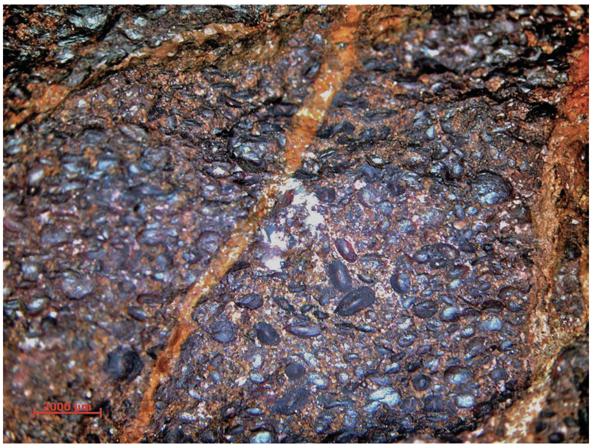

Fig. 5 – Lower Famennian OIS, Hodimont Formation, Lambermont (Belgium). Large hematitic ooids and flattened micro-oncoids in a red-stained carbonate matrix. Macroscopical view of rough surface. Scale bar is 2 mm.

Fig. 5 – OIS d'âge Famennien inférieur, Formation d'Hodimont, Lambermont (Belgique). Grandes ooïdes hématitiques et micro-oncoïdes plates dans une matrice carbonatée rougeâtre. Vue macroscopique d'une surface brute. Barre d'échelle : 2 mm.

dovician OIS of Normandy (very rare however), possibly indicating condensed deposits.

Microscopically, the Ordovician (Llanvirn) OIS of Normandy (basal part of the Urville Shales Formation) are characterized by rather homogenous and well-sorted, often flattened and fine-grained ferruginous "true" ooids (flaxseed type ore). Quite typical is the presence of alternating hematite and chlorite cortices of the ooids, and that of a sideritic-chloritic or fine-grained siliciclastic matrix (less frequent). The ooid size varies from 300 to 1000 microns (generally <500 micrometer). Hematitic ooids tend to be larger and either not deformed, or less deformed than the chloritic ooids. A detailed mineralogical analysis and an excellent microscopical description of the different ore facies can be found in Joseph (1982). Two main mineralogical facies can be recognized: a red hematitic oxide-facies (Fig. 2; Fig. 12-13) and a dark greenish-grey chlorite-carbonate facies (Fig. 3). Both resulted from superimposed sedimentary and diagenetic processes. Very conspicuous are the alternating mineralogies (so-called micro-sequences of chloritic and hematitic cortices) within the ferruginous ooids (Fig. 14). Chloritic ooids often show an external sideritic cortex. When visible, the nuclei are composed of single detrital quartz grains (Fig. 15), microcrystalline chlorite or large siderite crystals. The microfacies texture changes from a grain-supported to a matrix-supported fabric (oolitic grain-ironstones to oolitic pack- and wacke- ironstones). The cement consists either of chlorite, chlorite-hematite (with dispersed siderite rhombs) or siderite. Ferruginized sandstones with dispersed ferruginous ooid occur, as well as weathered OIS enclosing superficial limonitic (goethitic) crusts (Fig. 4-5).

Medium-sorted, fine- to (very) coarse-grained ferruginous hematitic pseudo-ooids (ferruginized rounded bioclasts) within a bioclastic limestone matrix ("fossil ore", Fig. 8-11) characterize the Lower-Middle Devonian boundary OIS beds (Heisdorf and Lauch Formations, Eifel Synclines). The grain size of the ferruginous allochems varies between 200 and 10000 microns, with an average size of < 1000 microns, the largest components being the ferruginized bioclasts and lithoclasts. True, concentrically built or superficial ferruginous ooids are rare or even lacking. Locally, large ferruginized sandstone clasts (lithoclasts) occur, as well as large ferruginized

Fig. 6 – Lower Famennian OIS, Hodimont Formation, Huy (Belgium). Mixed, "flax seed" ore and fossil ore facies. Medium-sorted hematitic coated grains and rounded bioclasts on a bedding surface. Macroscopical view of rough surface. Coin diameter is about 2,4 cm.

Fig. 6 – OIS d'âge Famennien inférieur, Formation d'Hodimont, Huy (Belgique). Minerai fossilifère mixte riche en ooïdes de type « graines de lin ». Vue macroscopique d'une surface brute. Barre d'échelle : 2,4 cm.

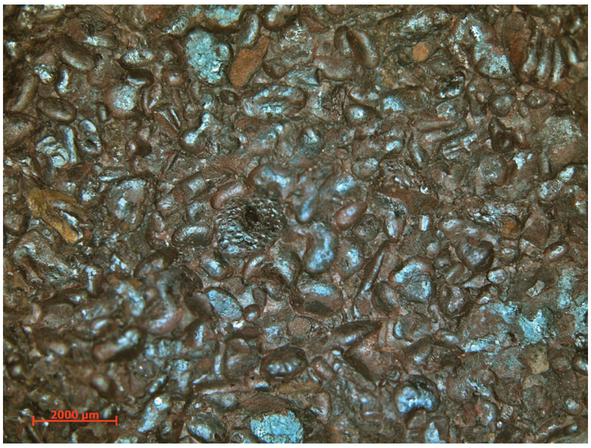

Fig. 7 – Lower Famennian OIS, Hodimont Formation, Vezin (Belgium). Heterogenous facies with numerous hematitic micro-oncoids, oncoids and small intraclasts. Macroscopical view of rough surface. Diameter of irregular intraclasts (left) is 8 mm.

Fig. 7 – OIS d'âge Famennien inférieur, Formation d'Hodimont, Vezin (Belgique). Faciès hétérogène à nombreuses micro-oncoïdes hématitiques, oncoïdes et petits intraclastes. Vue macroscopique d'une surface brute. Le diamètre des intraclastes irréguliers (gauche) est de 8 mm.

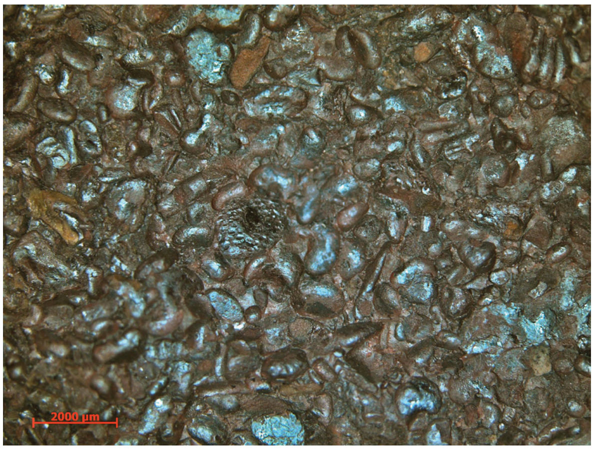

Fig. 8 – Emsian-Eifelian OIS, Heisdorf Formation, Hammermühle, Hillesheim (Germany). Coarse-grained, badly heterogenous hematitic OIS with ferruginized flattened bioclasts (“fossil ore”). Macroscopical view of rough surface. Scale bar is 2 mm.

Fig. 8 – OIS de l’Eifelien-Emsien, Formation d’Heisdorf, Hammermühle, Hillesheim (Allemagne). OIS hétérogène à grains grossiers et à bioclastes plats ferruginisés (« minerai fossilifère »). Vue macroscopique d’une surface brute. Barre d’échelle : 2 mm.

Fig. 10 – Emsian-Eifelian OIS, Heisdorf Formation, Oberahreck (near Blankenheim, Germany). Rounded lithoclast (exoclast) of ferruginized sandstone in coarse-grained, fossil ore-type OIS. Macroscopical view of rough surface. Scale bar is 1 cm.

Fig. 10 – OIS de l’Eifelien-Emsien, Formation d’Heisdorf, Oberahreck (près de Blankenheim Allemagne). Lithoclaste arrondi (exoclaste) de grès ferruginisé à l’intérieur d’un « minerai de fer fossilifère » grossier. Vue macroscopique d’une surface brute. Barre d’échelle : 1 cm.

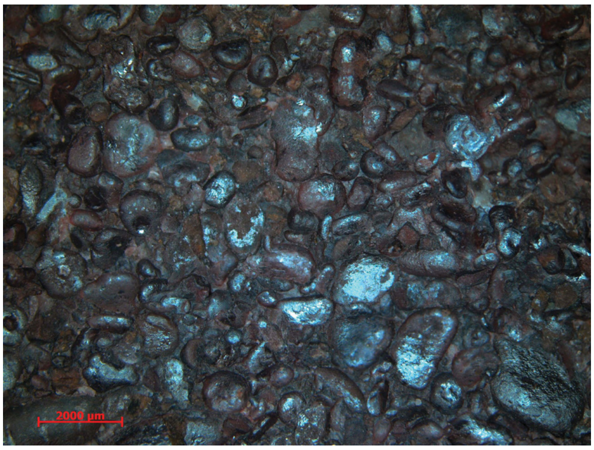

Fig. 9 – Emsian-Eifelian OIS, Heisdorf Formation, Hammermühle, Hillesheim (Germany). Detail of previous photograph: flattened and rounded ferruginized (hematitic) bioclasts. Scale bar is 2000 µm.

Fig. 9 – OIS de l’Eifelien-Emsien, Formation d’Heisdorf, Hammermühle, Hillesheim (Allemagne). Détail de la figure 8 : bioclastes ferruginisés hématite) roulés et plats. Barre d’échelle : 2000 µm.

Fig. 11 – Emsian-Eifelian OIS, Heisdorf Formation, Hammermühle, Hillesheim (Germany). Large, ferruginized (hematitic) oncoid, showing laminated texture. Fossil ore facies. Macroscopical view of rough surface. Scale bar is 1 cm.

Fig. 11 – OIS de l’Eifelien-Emsien, Formation d’Heisdorf, Hammermühle, Hillesheim (Allemagne). Grand oncoïde ferruginisé (hématite). « minerai de fer fossilifère ». Vue macroscopique d’une surface brute. Barre d’échelle : 1 cm.

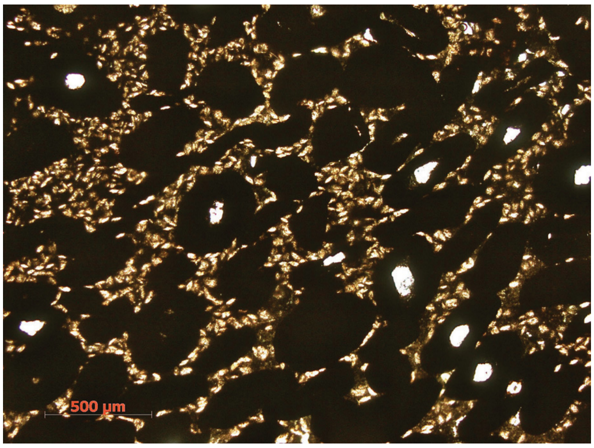

Fig. 12 – Sample May X. Urville Shales Formation. Oxide-facies. Pack- to grain-ironstone with hematitic ooids (detrital quartz grains as nuclei) and sideritic matrix. Micrograph of thin section in transmitted polarized light without crossed polarizers. Scale bar is 500 microns.
Fig. 12 – Échantillon May X. Formation des Schistes d'Urville. Faciès oxydé. Texture « packstone » à « grainstone » avec ooïdes hématitiques (nucléus constitué de grains de quartz détritique) et matrice de sidérite. Microphotographie de lame-mince prise en lumière transmise 1x polarisée (= lumière naturelle). Barre d'échelle : 500 µm.

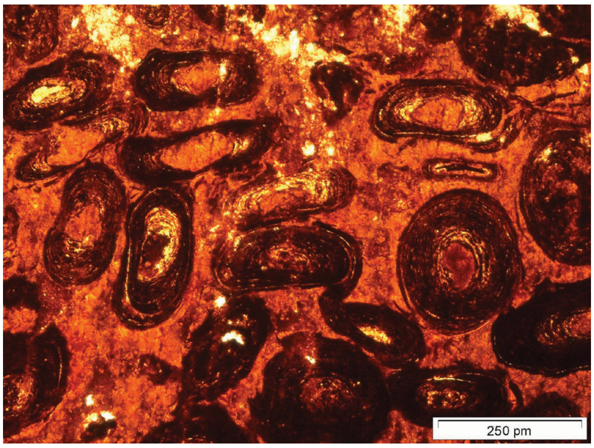

Fig. 13 – Sample Urville X. Detail of oxide facies. Urville Shales Formation, Flattened and locally deformed hematitic ooids. Grain-ironstone with hematitic cement. Micrograph of thin section in transmitted polarized light, without crossed polarizers. Scale bar is 250 microns.
Fig. 13 – Échantillon Urville X. Détail du faciès oxydé. Formation des Schistes d'Urville. Ooïdes hématitiques plates et localement déformées. Texture « grainstone » avec ciment. Microphotographie de lame-mince prise en lumière transmise 1x polarisée. Barre d'échelle : 250 µm.

oncoids and intraclasts (Fig. 16). The microfacies texture is essentially grain-supported, producing bioclastic (pseudo-oolitic) pack-ironstones and grain-ironstones (Fig. 17), locally grading into bioclastic/pseudo-oolitic rud-ironstones (Fig. 18). A petrographical differentiation between OIS from the succeeding Heisdorf and Lauch Formations is more difficult. However, the OIS from the Lauch Formation contain less ferruginized and less densely packed pseudo-ooids (mainly hematite-impregnated crinoid ossicles). The Lauch OIS correspond to loosely packed, pseudo-oolitic iron-grainstones of which the cement is locally sideritized. However, a better distinction between the Heisdorf and Lauch OIS is possible based on geochemical criteria (e.g. the Sr/Ca ratio, according to A. Katsch in Goemaere *et al.*, this book) reflecting differences in depositional setting (paleobathymetry).

Finally, the late Upper Devonian (Famennian) ironstone deposits (Hodimont Formation, Famenne Shales Group) of the Ardennes in Belgium,

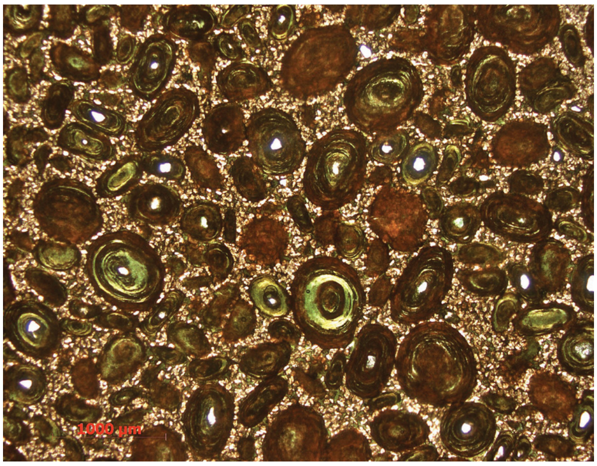

Fig. 14 – Sample SGLV. Urville Shales Formation. Chloritic-carbonate facies with chloritic ooids and sideritic matrix/cement. Oolitic pack- to grain-ironstone. Notice alternating mineralogies of cortices. Micrograph of thin section in transmitted polarized light, without crossed polarizers. Scale bar is 1000 µm.
Fig. 14 – Échantillon SGLV. Formation des Schistes d'Urville. Faciès carbonaté et chloritique avec ooïdes chloriteuses et ciment/matrice sidéritique. À noter les alternances minéralogiques dans le cortex. Microphotographie de lame-mince prise en lumière transmise 1x polarisée. Barre d'échelle : 1000 µm.

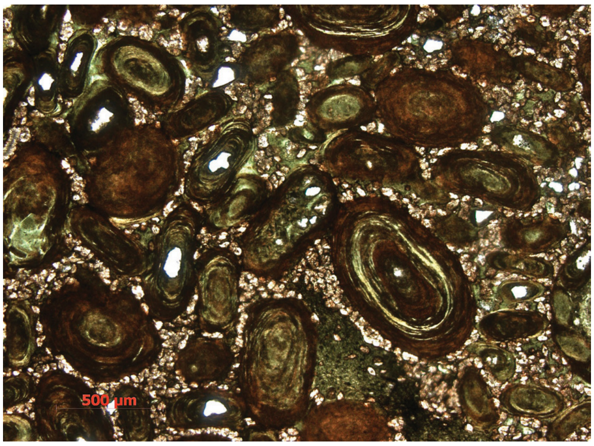

Fig. 15 – Detail of previous micrograph (Fig. 14). Note quartz nuclei in the ooidsand patche of chloritic matrix. Scale bar is 2000 µm.
Fig. 15 – Détail de la microphotographie précédente (Fig. 14). On notera le nucléus de quartz dans les ooïdes et les taches chloriteuses de la matrice. Barre d'échelle : 500 µm.

Fig. 16 – Oberahreck, sample OBA-01: Heisdorf Formation (Germany), bioclastic iron-grainstone with intraclasts and lithoclasts. Ferruginized bioclasts consists of crinoid ossicles , bryozoans, brachiopod shells, etc. Micrograph of thin section in transmitted polarized light, without crossed polarizers. Scale bar is 1 mm.
Fig. 16 – Oberahreck, échantillon OBA-01: Formation d'Heisdorf (Allemagne), grainstone ferrifère bioclastique à intraclastes et lithoclastes. Les bioclastes ferruginisés sont constitués d'articles de crinoïdes, de bryozoaires, coquilles de brachiopodes, etc. Microphotographie de lame-mince prise en lumière transmise 1x polarisée. Barre d'échelle : 1 mm.

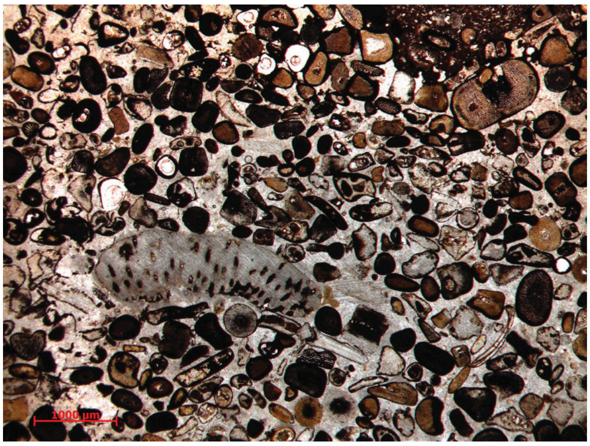

Fig. 17 – Oberahreck, sample OBA-09: Lauch Formation (Germany). Pseudo-oolitic iron-grainstone mainly composed of hematite-impregnated skeletal grains (dominant crinoid ossicles). Micrograph of thin section in transmitted polarized light, without crossed polarizers. Scale bar is 1 mm.
Fig. 17 – Oberahreck, échantillon OBA-09: Formation de Lauch (Allemagne). Grainstone ferrifère pseudo-oolithique principalement constitué de grains squelettiques (articles de crinoïdes dominants) imprégnés d'hématite. Microphotographie de lame-mince prise en umière transmise 1x polarisée. Barre d'échelle : 1 mm.

consist of well- to medium-sorted heterogeneous, fine- to medium-grained, pure or mixed flaxseed- and fossil ore-type hematitic oolitic ironstones in siliciclastic and/or carbonate matrices (Fig 6-7, 20-21). Several distinct stratigraphic levels do exist within the Famennian of the Namur, Dinant and Vesdre Synclinoria. However, only the lowermost Famennian one has been mined as an iron ore. Within some of the stratigraphically younger Famennian oolitic ironstone levels, proximal and distal facies can be distinguished on the basis of microfacies differences and mineralogy of the ferruginous pseudo-ooids (Dreesen, 1989). Only the proximal hematitic facies of the lowest stratigraphical oolitic ironstone level (level I of Dreesen, 1989) is supposed to have been used in prehistoric times for the manufacturing of ochre. Their grain size varies here between 200 and 5000 microns, with an average < 500 microns, the largest components being micro-oncoids, intraclasts and rip-up clasts of ferruginized microstromatolitic hardgrounds. The latter are exceptional and their

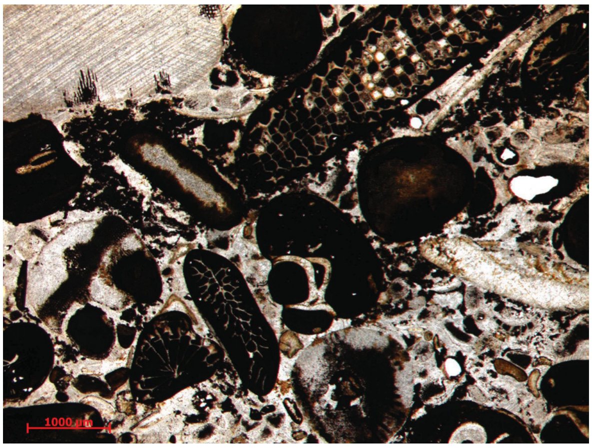

Fig. 18 – Sample HAM-01. Hammermühle. Heisdorf Formation. Badly sorted, coarse-grained fossil ore facies. Pseudo-oolitic iron-grainstone / iron-rudstone with large ferruginized skeletal grains (crinoid ossicles, bryozoans). Micrograph of thin section in transmitted polarized light, without crossed polarizers. Scale bar is 1 mm.
Fig. 18 – Échantillon HAM-01. Hammermühle. Formation d'Heisdorf. Faciès fossilifère à grains grossiers, mal classé. Grainstone ferrifère pseudo-oolithique / rudstone ferrifère à grands grains ferrugineux du squelette (articles de crinoïdes, bryozoaires). Microphotographie de lame-mince prise en lumière transmise 1x polarisée.
Barre d'échelle : 1 mm.

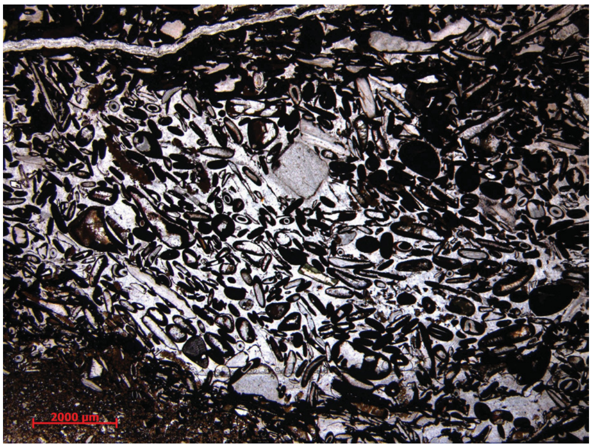

Fig. 20 – Sample 155-E1. Hodimont Formation. Proximal facies. Densely packed ferruginized skeletal grains and rare ooids. Pseudo-oolitic grain-ironstone. Micrograph of thin section in transmitted polarized light, without crossed polarizers. Scale bar is 2 mm.
Fig. 20 – Échantillon 155-E1. Formation d'Hodimont. Faciès proximal. Grains ferruginisés squelettiques et densément compactés avec rares ooïdes. Grainstone ferrifère pseudo-oolithique. Microphotographie de lame-mince prise en lumière transmise 1x polarisée.
Barre d'échelle : 2 mm.

size may exceed a few cm. Diagenetic sideritisation and dolomitisation, particle deformation as well as sulphide mineralisations, affect most of the studied Famennian OIS. However, the intensity of these mineralisations varies strongly (even within the same deposit) and depends on local tectonics. Microfacies texture is strongly varying from condensed ("lean") oolitic grain-ironstones, to bioclastic (pseudo-oolitic) grain- and pack-ironstones and mixed facies in proximal settings. In more distal settings, dispersed pseudo-oolitic/bioclastic grain-ironstones occur displaying a higher chamosite/hematite ratio. All microfacies types can be "clean" or contaminated by siliciclastics (silt- or sand-sized grains of detrital quartz and other silicates).

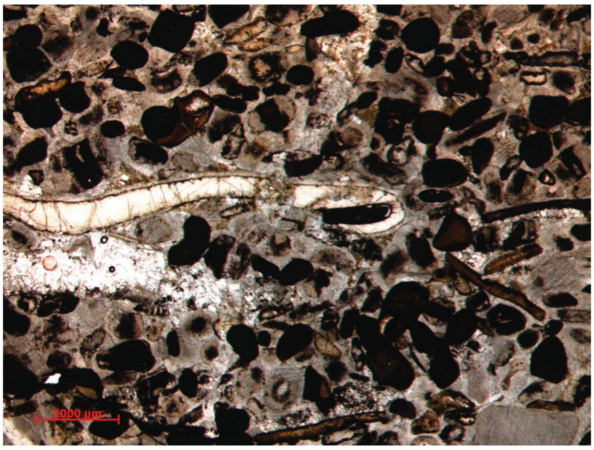

Fig. 19 – Sample BEL-1., Heisdorf Formation. Fossil ore facies (hematite-impregnated skeletal grains – mainly crinoid ossicles) with large trilobite fragments. Pseudo-oolitic grain-ironstone. Micrograph of thin section in transmitted polarized light, without crossed polarizers. Scale bar is 1 mm.
Fig. 19 – Échantillon BEL-1, Formation d'Heisdorf. Faciès fossilifère (grains squelettiques imprégnés d'hématite – principalement des articles de crinoïdes) avec grands fragments de trilobite. Grainstone ferrifère pseudo-oolithique. Microphotographie de lame-mince prise en lumière transmise 1x polarisée. Barre d'échelle : 1 mm.

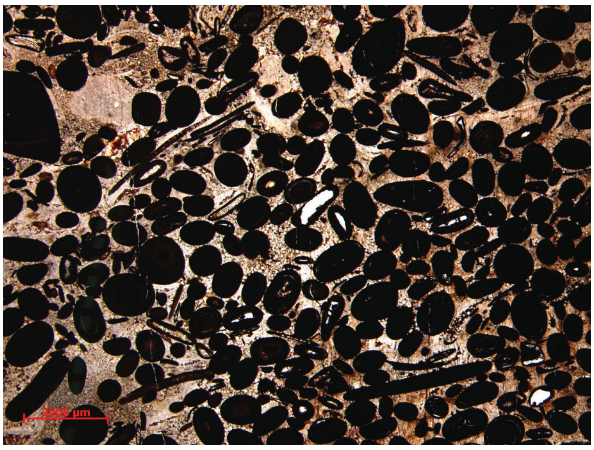

Fig. 21 – Sample Sclaigneaux-1. Sclaigneaux (Andenne). Hodimont Formation. Proximal facies. Oolitic grain-ironstone. Mixed oolitic-pseudo-oolitic facies: hematitic ooids (dominant) with hematite-impregnated/coated elongated skeletal grains. Micrograph of thin section in transmitted polarized light, without crossed polarizers. Scale bar is 2 mm.

Fig. 21 – Échantillon Sclaigneaux-1. Sclaigneaux (Andenne). Formation d'Hodimont. Faciès proximal. Grainstone ferrifère oolithique. Faciès mixte oolithique-pseudo-oolithique : ooïdes hématitiques (dominant) avec des grains squelettiques allongés et revêtus/imprégnés d'hématite. Microphotographie de lame mince prise en lumière transmise 1x polarisée. Barre d'échelle : 2 mm.

Furthermore, a clear distinction can be made between the Eifelian and Belgian fossil iron ores, based on the nature of the ferruginized bioclasts and other components. Eifelian OIS contain ferruginized bioclasts (crinoids, bryozoans, trilobites, brachiopods, goniatites, see Fig 19)) and ferruginized siliciclastic lithoclasts, whereas the Famennian OIS are dominated by ferruginous ooids and algal micro-oncoids (Fig. 22), locally mixed with ferruginized bioclasts (including crinoids, bryozoans, brachiopods, ostracods, algae and microfossils of uncertain origin) and locally intraclasts (e.g. ferruginized stromatolitic crusts; Fig. 23). Distal facies of the Famennian OIS contain slightly Fe-impregnated skeletal grains only, such as crinoid ossicles and ostracods (Fig. 24), and display a higher chlorite/hematite ratio, probably related to density separation during storm-induced transport (Dreesen, 1989).

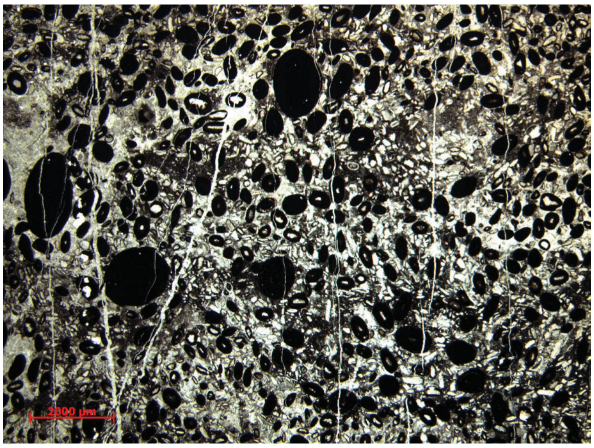

Fig. 22 – Sample Verviers VRD-27-2. Hodimont Formation. Distal facies. Hematitic ooids and micro-oncoids. Oolitic pack- to grain-ironstone. Micrograph of thin section in transmitted polarized light, without crossed polarizers. Scale bar is 2 mm.

Fig. 22 – Échantillon Verviers VRD-27-2. Formation d'Hodimont. Faciès distal. Ooïdes hématitiques et micro-oncoïdes. Packstone à grainstone oolithique ferrugineux. Microphotographie de lame-mince prise en lumière transmise 1x polarisée. Barre d'échelle : 2 mm.

5 ARCHEOLOGICAL MATERIALS

A series of thin sections has been made from archeological objects (red ochre) found in Normandy and in the Hesbaye area of Belgium. These allow a preliminary comparative petrographical analysis aimed at tracing their probable geological and geographical provenance. All archeological objects (hematite pencils or crayons) found in Normandy were derived from regional geological sources (Ordovician OIS from the Urville Shales Formation). The same statement can be made for the Belgian archeological objects found in the Hesbaye area, where a regional source (the proximal facies of the Lower Famennian OIS from the Hodimont Formation) has been identified.

Archeological findings of red ochre (OIS) from LBK-settlements (Graetheide and Caberg) in the Dutch province of Limburg (The Netherlands) have recently been macroscopically and geochemically analyzed: although different geological types of source material were identified (OIS and ferruginized siliciclastics), there is no evidence provided for their exact geological or

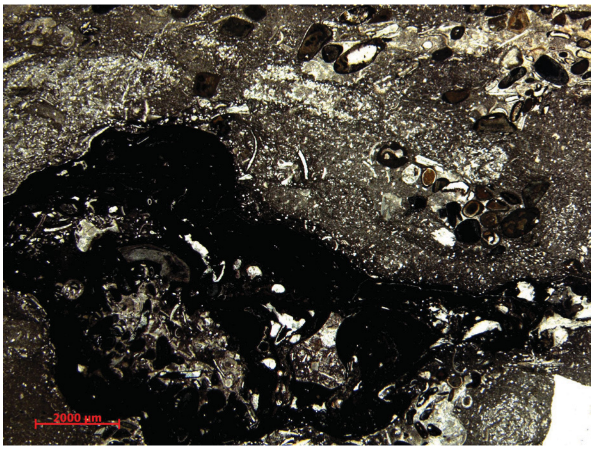

Fig. 23 – Sample Limbourg-2. Hodimont Formation. Distal facies. Hematite-impregnated algal oncoid, hematitic/chloritic rounded skeletal grains and superficial ooids in a bioclastic packstone-grainstone. Bioclastic pack-ironstone. Micrograph of thin section in transmitted polarized light, without crossed polarizers. Scale bar is 1 mm.
Fig. 23 – Échantillon Limbourg-2. Formation d'Hodimont. Faciès distal. Oncoïde alguaire imprégnée d'hématite, grains squelettiques arrondis et constitués d'hématite/chlorite et ooïdes superficielles dans un packstone-grainstone bioclastique. Microphotographie de lame-mince prise en lumière transmise 1x polarisée. Barre d'échelle : 1 mm.

geographical provenance (Wijnen, 2013).

Robroeks *et al.* (2012) reported the use of red ochre (hematite) by early Neanderthals in the Maastricht-Belvédère excavations (The Netherlands). The authors tentatively indicated both the Liège-Dinant-Namur area in Belgium and the Eifel area in Germany as potential source areas for the materials used. Based on the existence of a known transfer of flint artifacts from the Maastricht Cretaceous chalk area to the East Eifel sites of Wannen and Schweinkopf, the Eifel area is suggested as hypothetical provenance area as the hematite material (OIS?) might well have travelled in the opposite direction.

Although archeological evidence for an iron-industry in the Eifel area is present at least since the Iron Age (Halstatt) near Hillesheim and during Roman times near Ahrweiler, there is no real evidence for the use of particular levels of Eifel OIS (Kronz, 2003).

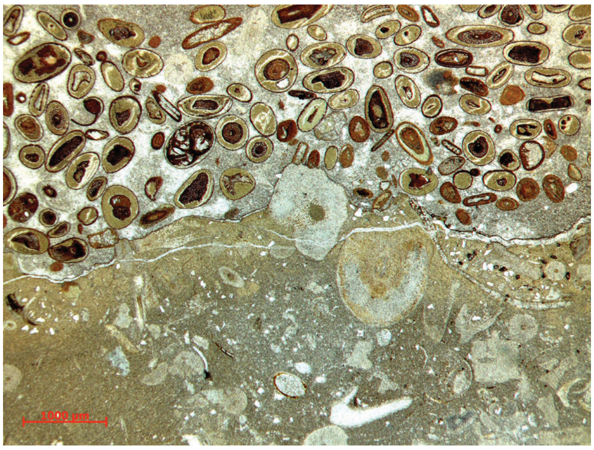

Fig. 24 – Sample Hamoir-Tohogne-5-2. Distal facies. Bioclastic grain-ironstone with ferruginized ooids and pseudo-ooids: ferruginzied ooids with chloritic cortices around hematitic rounded skeletal grains (mainly crinoids) and superficial ooids. Note presence of basal erosional unconformity. Micrograph of thin section in transmitted polarized light, without crossed polarizers. Scale bar is 1 mm.
Fig. 24 – Échantillon Hamoir-Tohogne-5-2. Faciès distal. Grain-ironstone bioclastique avec des ooïdes ferrugineuses et des pseudo-ooïdes: ooïdes ferrugineuses avec cortex chloritique autour des grains arrondis hématitisés (principalement des crinoïdes) et des ooïdes superficielles. Notez la présence d'une surface érosive (non-conformité). Micrographie d'une lame-mince observée en lumière 1x polarisée. Barre d'échelle : 1 mm.

6. CONCLUSIONS

Oolitic ironstones (OIS) represent a major iron source worldwide and an important historical raw material. Moreover, OIS have been used for the manufacture of red ochre, at least since Paleolithic times. The first results of a comparative petrographical analysis of geological samples of OIS from the Paleozoic of Normandy (France), Belgium and the Eifel (W-Germany) are discussed. Different oolitic ironstone types can be roughly identified on the basis of their main components (grains) and the mineralogy of the iron-bearing minerals. Furthermore, microfacies analysis can be applied to differentiate between macroscopically analogous OIS. Our results generally confirm the outcome of geochemical studies that have been conducted simultaneously

	Ordovician OIS	*Famennian OIS Proximal facies*	*Famennian OIS Distal facies*	*L-M Devonian OIS - Eifel*
Real ooids	XXX	XXX	X	X
Pseudo-ooids	0	XX	XX	XX
Rounded bioclasts	0	XX	XX	XXX
Pisoids	0	XX	0	0
Oncoids	0	X	0	X
Intraclasts	X	X	X	X
Lithoclasts	0	X	0	XX
Microstromatolithes	X	X	0	0
Cortex mineralogy	alternating H-C-S	H>C (S)	C>H	H (S)
Nucleus	Q, C	Q, fossil	fossil	fossil
Grain size	small (<500)	variable	variable	variable
Grain sorting	excellent	bad to good	medium-good	medium-good
Matrix	siliciclastic	Siliciclastic/carbonate	carbonate	carbonate
Cement	HEM-CHL-SID	HEM-CHL-SID-DOL, Fe-CAL	Fe-CAL, SID	Fe-CAL, SID
Grain supported	0	X	X	X
Matrix supported	X	X	0	0
Bioturbation	X	X	X	0

Tab. 2 – Overview of the results of a comparative microfacies analysis of the studied OIS based on thin sections microscopy. Relative frequencies (estimations) of the components are indicated by symbols: 0 (totally absent), X (present), XX (common) and XXX (very frequent or abundant). Mineralogy includes: H or HEM (hematite), C or CHL (chlorite), DOL (dolomite), S or SID (siderite), CAL (calcite), Fe-CAL (ferruginous calcite), Q (detrital quartz grain).

Tab. 2 – Synthèse des résultats comparatifs des analyses pétrographiques (sur lames-minces) des microfaciès des niveaux d'OIS étudiés. Les fréquences relatives (estimations) des constituants sont indiquées par des symboles : 0 (totalement absent), X (présent), XX (commun), XXX (très fréquent ou abondant). Les minéraux comprennent : H ou HEM (hématite), C or CHL (chlorite), DOL (dolomite), S ou SID (sidérite), CAL (calcite), Fe-CAL (calcite ferrifère), Q (grains de quartz détritique).

on the same materials (see other chapters in this book): regional sources of OIS have been identified both for the archeological findings in the LBK-settlements of Normandy and in Belgium.

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