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THEMATIC ISSUE

Geochemical characterization of "Lorraine limestones" from the Saint-Paul Cathedral of Liège (Belgium): assumptions for the true provenance of the building stones

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Abstract

We investigate the provenance of the ochre building stones called "Lorraine limestones" used for architectural specific elements of the Saint-Paul Cathedral in Liège (Belgium) between the thirteenth and fifteenth century. A multi-analytical approach, including archives study, petrography and Rare Earth Elements geochemistry, has been performed to characterize the stones used in the church and to compare them with ochre limestones outcropping in the north-east of the Paris Basin. Our study suggests that a very restricted geographical area near the ancient port of Donchery (Ardennes, France) including Dom-le-Mesnil and Hannogne ancient quarries of Bajocian limestones (Middle Jurassic) should clearly be regarded as the potential origin location for the stones used in the Saint-Paul Cathedral.

Keywords Cultural heritage · Limestone · Provenance · Petrography · Geochemistry · Rare earth elements

Introduction

Deciphering the provenance of building stones during the Historical Times remains a challenge. However, this is particularly relevant for three reasons : first, our knowledge of the commercial relationships (Rolett et al. 2015), second, for a better comprehension of supply strategies of ancient construction crafts, linked to economical, technical and aesthetic challenges (Wilkinson et al. 2008; Barra et al. 2009; Brennan et al. 2013; Columbu et al. 2014), and finally the potential use of appropriate stones during restoration of the buildings (Coli et al. 2008; Turmel et al. 2014; Hopkinson et al. 2015). In the last decades, several methods were applied to Belgian limestones to determine/refine the areas/localities of extraction of stones (e.g. Groessens 1991; Dreesen et al. 2003; Dreesen and Dusar 2007; Storemyr et al. 2007; De Kock et al. 2015, 2017). Both petrography and geochemistry of Rare Earth Elements (REE) were already applied to Jurassic stones in France (e.g. Comblanchien limestones from Burgondy, Malfilatre et al. 2012) to establish the links between the mining and the building areas, and to refine our knowledge of historical supply strategies. Here we aim at bringing new petrographical and geochemical data to identify the provenance of several samples of "Lorraine limestones" used in the St Paul Cathedral in Liege between the beginning

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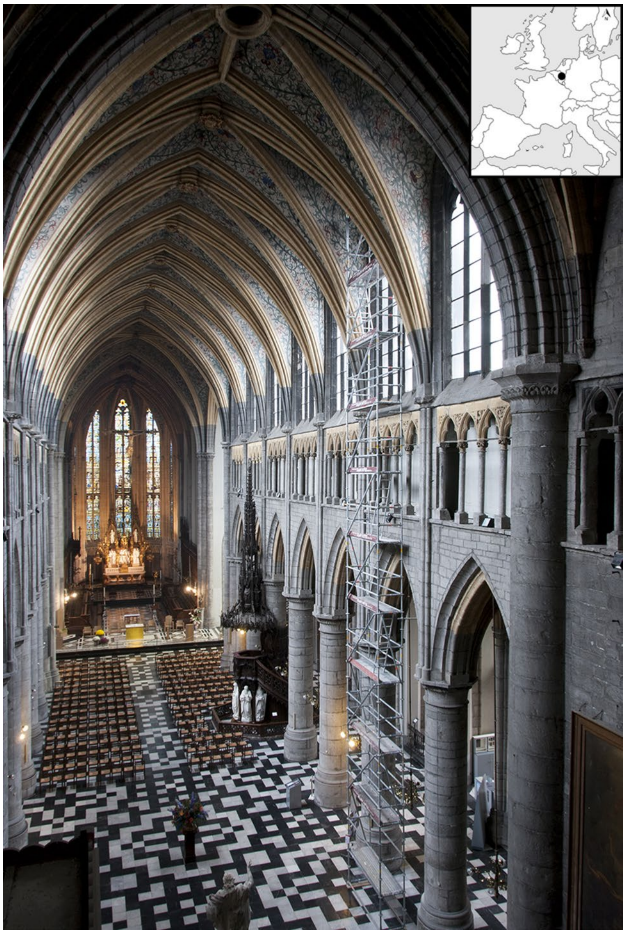

Fig. 1 Choir of Saint-Paul Cathedral of Liège (Belgium), with grey Mosan limestones and at the top, ochre the so-called "Lorraine limestones"

of the thirteenth and the end of the fifteenth centuries. The Saint-Paul Cathedral was built using three kinds of stones (Dewez and Forgeur 1980): the grey Mosan limestones, the ochre so-called "Lorraine limestones" and the grey to white "Tuffeau" from the Maastricht area. The origin of the Mosan limestone should be found in the numerous quarries of the Mosan valley around Liège. Alternatively, no ochre limestones can be found in the neighborhood of Liège. Previous study (Forgeur 1992) attributes a French provenance from Lorraine area for these stones, which were brought to Belgium using the Meuse River, around 150–200 km away.

Historical and archaeological background

The Saint-Paul collegiate church is a gothic building erected in different campaigns to replace an older Ottonian church, probably built during the tenth century (Forgeur 1959, 159). Like in most cases in the Middle Age, the reconstruction began by the Eastern part. Choir (Fig. 1), transept and the last two bays of the nave belong to the same campaign, whose carpentry has been dated by dendrochronology from 1251 to 1252d.[1] The construction of the nave carried on, to the West, with the next two bays, dated from 1290 to 1300d. In the first decades of the fourteenth century, the nave was achieved, with the construction of the three western bays (1328–1330d) and the choir was transformed: the original flat chevet was removed and replaced by a narrow bay combined with a polygonal apse, flanked by two small-oriented chapels (Hoffsummer et al. 2005). The chantries of the nave were erected in the fourteenth century (north chapels) and the fifteenth century (south chapels) (Forgeur 1959, 177–183). At the Western extremity, the tour of the church was built from 1391 and during the fifteenth century. It was left uncompleted until the nineteenth century, before the construction of the bell tower.

Until the end of the thirteenth century, the Lorraine limestones were just used for specific elements of the architecture: upper part of the arcades, capitals and spandrels of the triforium, ribs and keystones. These uses highlight the technical advantages of this material: softer than the Mosan limestones, the Lorraine limestones fit much better to the sculpture and are reserved in consequence for the building's finest parts. Their density, lower than those of the Mosan limestones, probably also explains the selection of this material for the upper parts of the architecture. Particularly, they are used for the ribs of the vaults, which support vaulting cells in Tuffeau stones from Maastricht area. This specific selection of the Lorraine limestones was still in use in the first third of the fourteenth century for the edification of the three first bays of the nave. However, the numerous blocks of Lorraine limestones in the walls, transoms and supports of the choir apse and of the two eastern chapels erected around 1328–1330 stress the increasing use of soft limestone for more common parts of the architecture. This trend is still more impressive in the chantries of the nave, dated from the fourteenth or fifteenth century. This evolution can also be observed in the chantries of the church of the Holy Cross in Liège, from the very end of the fourteenth century (Piavaux 2013, 196–198), and on the external wall of the choir of the Saint Denis church, dated around 1425–1430 (Hoffsummer 1999, 42). Though, elsewhere in the Meuse valley, the Lorraine limestones were still sparingly used during the fourteenth and fifteenth centuries, following the specific uses of the previous centuries. The increasing importance of the Lorraine limestones on the building sites of Liège, whereas this city is the most distant of the extraction area of these exogenous materials revealed privileged trade

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[1] A « d » following a date means that this date has been obtained by dendrochronology.

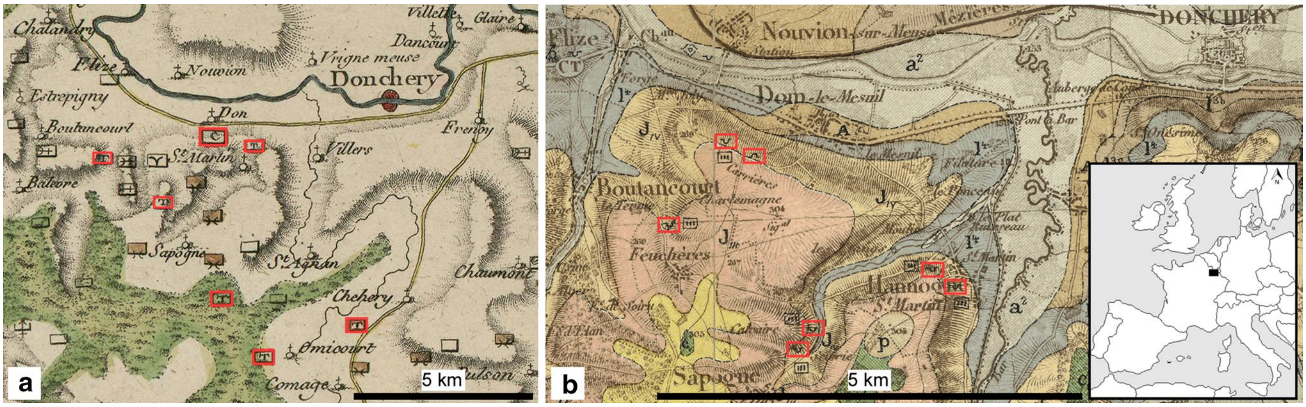


Fig. 2 Old mineralogical and geological maps (**a**: from Guettard and Monnet 1780; **b**: from; Gosselet and Nivoit 1888). Red rectangles show the building stone quarries located in the Bajocian ochre limestones near Donchery (Ardennes, France). Distance between Dom-le-Mesnil (Don) and Donchery around 5 km

during this period between ecclesiastic builders of the Episcopal city and the quarries of soft limestone located in the Haute Meuse region.

Some details about these trades and about the location of quarries are to be found in archival texts of the St Lambert Cathedral. These sources spring from the fabric (*opus ecclesiae*) and were produced between 1372 and 1480. Texts from the end of the fourteenth century mention the transport of stones quarried in Donchery and the surrounding places until Liège, by Gérard Habran, a boatman of Mézières. This trader is quoted in the texts of 1372 and 1385 and he consequently seems to be the official supplier of the fabric for a long time (Schoolmeesters 1914). The text of 1385 is particularly explicit on the motivations of these purchased stones: the builders need the same type of soft stones and already squared. These criterions, reminded to denounce the inferior quality of some supplied lots, bring out the advantages of the Lorraine limestone, concerning carved ornament and moulded elements above all.

In the geological Atlas and maps from the eighteenth and nineteenth centuries, some building stone quarries of limestone are located near the Meuse, downstream from Donchery (Fig. 2). The « *Atlas et description minéralogiques de la France* », published in 1780 (Guettard and Monnet 1780) briefly describes the stones of this area and highlights the importance of the Don quarries as source of building materials. More precisely, the map no 17 (Fig. 2a) shows the importance of Don quarry district for the extraction, with seven quarries of dimensional stones [T] and limestones (C): Don (two quarries), Boutancourt, Sapogne, Saint-Martin, Chéhery and Omicourt. That is the largest amount of dimensional stone quarries in all the covered area. At nearly the same period, the Cassini's map of Charleville-Mézières area (Cassini de Thury 1760) shows one quarry located near Dom-le-Mesnil and another near Hannogne-Saint-Martin, but with no further information about the kind of quarried stone.

In 1842, Sauvage and Buvignier published a lot of details on the various kinds of geological resources of this area and on the quality of the Dom-le-Mesnil soft limestone (Sauvage and Buvignier 1842, 325, 506), noticing that around ten quarries existed in Dom and that some equivalent quarries could be found near villages of Boutancourt, Feuchères, Saint-Martin, Saint-Walfroy, Cheveuge and Servion. Moreover, the Dom area, which included Dom-le-Mesnil, Boutancourt, Sapogne-and-Feuchères, and Hannogne-Saint-Martin, seem to have been the most important quarry centre. Lately, on the "modern" geological maps (Fig. 2b from Gosselet and Nivoit 1888) and in inventories from the end of the nineteenth century (Durand-Claye and Debray 1890), some quarries of soft limestone were still located in these villages, and with twelve active quarries of dimensional stones, Dom-le-Mesnil still remains the main quarry centre in French Ardennes area.

This quarry district of Dom-le-Mesnil can also be identified in few texts of the St Lambert cathedral—belonging to the accounts of the fabric—and written at the end of the fifteenth century. In 1476 and 1480, the fabric bought lots of stones from « *Mézières, Dun and Donchery* » (Poncelet 1934, 25, 27; Forgeur 1992, 68). The paleography favours rather the reading « Dun », a term that would correlate with Dun-sur-Meuse, in the Lorraine area. But the surroundings of this locality contain white limestones from Oxfordian layers that are quite different from the ochre limestones observed in Liège's buildings and are apparently completely unknown in the gothic building sites of the Middle Meuse valley. As a consequence, the mention of "Dun" in this text, instead of "Don", would probably result from a mistake of the fifteenth century scribe. And this mention leads to another mistake 400 years later. This wrong attribution

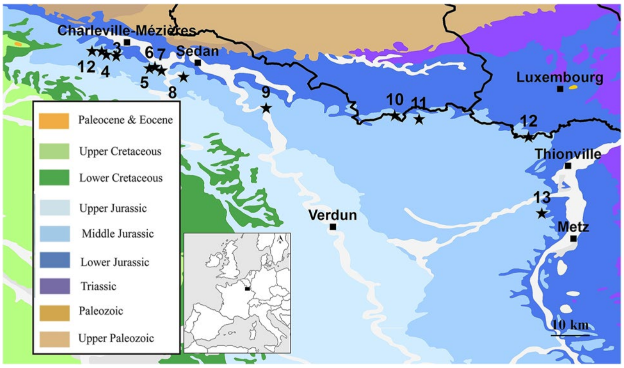


Fig. 3 Simplified geological map (from http://portal.onegeology.org) and location of sampling sites in the Bajocian of the Paris Basin. 1: Neuville-les-This (France); 2:Fagnon (France); 3: Warnécourt (France); 4: Evigny (France); 5: Dom-le-Mesnil (France); 6: Sapogne-et-Feuchères (France); 7: Hannogne-Saint-Martin (France); 8: Cheveuges (France); 9: Inor (France); 10: Grandcourt (Belgium); 11: Tellancourt and Pas-Bayard Quarry, Cons-la-Grandville enclave (France); 12: Rumelange (Luxembourg); 13: Jaumont - Malancourt-la-Montagne (France)

to Dun-sur-Meuse (in Lorraine area) realized without any comparative observations between the stones from the monument and quarries probably guided the historian to call the ochre stones used in Liège Cathedrals as “Lorraine limestone”.

Materials and methods

Seven samples were collected from distinct parts of Saint-Paul Cathedral using a small chisel and a small drill, either from hidden parts or from already deteriorated parts of the church to minimize the damages. In addition, 85 fragments of yellow–ochre limestones were sampled from a selection of 13 quarries in France, Belgium and Luxembourg (Fig. 3). These limestones are coming from various Bajocian and Bajocian/Bathonian formations (Middle Jurassic). According to outdoor observations in the monument and to the study of archives, only clear yellow to ochre true limestones were sampled, avoiding the sandy limestone from Lower Jurassic (Sinemurian) and the white limestones from Middle and Upper Jurassic (e.g. in upper Bathonian and Oxfordian).

One part of each sample was finely crushed in a RETSCH PM 100 planetary ball mill or manually in an agate mortar (when the amount of material was not sufficient to use a mill) to obtain the maximum 125 µm granulometry, and thin sections were made from the remaining part of the samples. Analyses have been performed for 61 chemical elements in the Activation Laboratories (Ontario, Canada). REE and most of the trace elements have been analysed by Fusion Mass Spectrometry (FUS-MS, Perkin Elmer Sciex Elan 9000 ICP-MS; Sciex AB, Singapore), Sr, Ba, Zr V, and major elements by Fusion Inductively Coupled Plasma Optical Emission Spectrometry (FUS-ICP, Varian Vista 735 ICP; Agilent, Santa Clara, CA, USA). The geochemical results were normalized using the PAAS reference shale (*Post Archean Australian Shale*; McLennan 1989). When comparing the contents in Rare Earth Elements (REE), the Ce anomaly was calculated with the formula:

$$\frac{\mathrm{Ce}}{\mathrm{Ce}*} = \mathrm{Ce}\sqrt{\mathrm{La} * \mathrm{Pr}}$$

proposed by Akagi and Masuda (1998). The thin sections were analysed using a petrographic microscope, Olympus BX-61, linked to a CCD camera (Qicam Fast 1384 from QImaging).

Because this article focuses on the interest of REE patterns to discriminate building stone provenances, we do not present all the results of the chemical analysis, but these results are given as supplementary data (Table 1). New measurements (such as colours, porosity) are still in progress and will lead to a complete multivariate analysis of these limestones.

The location of the sampling sites in the church was chosen to represent various building phases (Fig. 4). STP1 is a piece of column taken in the third north side chapel. STP2 is a piece of column taken in the sixth north side chapel. STP3 is a piece of the abacus of a capital in a south chapel. STP4 is a piece of jamb taken in the third south side chapel. STP5 is a piece of the triforium taken in the south transept, and STP6 and STP7 are pieces of the triforium, taken in the south part of the nave. STP5 belongs to the 1251–1252 building period, STP2 and STP6 belong to the 1290–1300 building period, STP1, STP3 and STP7 belong to the 1328–1330 building period, and STP4 belongs to the fifteenth century building period.

The quarries were chosen because of (1) the macroscopic similarity of their stones with those of the cathedral, (2) their proximity to the Meuse River, and (3) the fact that they were previously suggested to have supplied dimensional or at least building stones (see above). The search of the different sampling sites was based on ancient and new topographic and geological maps as well as on archives dealing with ancient quarries in France (Guettard and Monnet 1780; Durand-Claye and Debray 1890; Noel 1970). Where the quarry face was well preserved or still exploited, we collected several samples from several layers of the same section. That was the case in Dom-le-Mesnil, Hannogne quarries, the two main sites in our study area and in Grandcourt quarry. In the other quarries or outcrops, only three isolated, in situ samples were collected.

An important underground quarry is located in the highest part of Dom-le-Mesnil, in the French Ardennes area (N49°41′02″ E4°47′56″), a village close to the Meuse, with numerous old and recent quarries of dimensional stones.

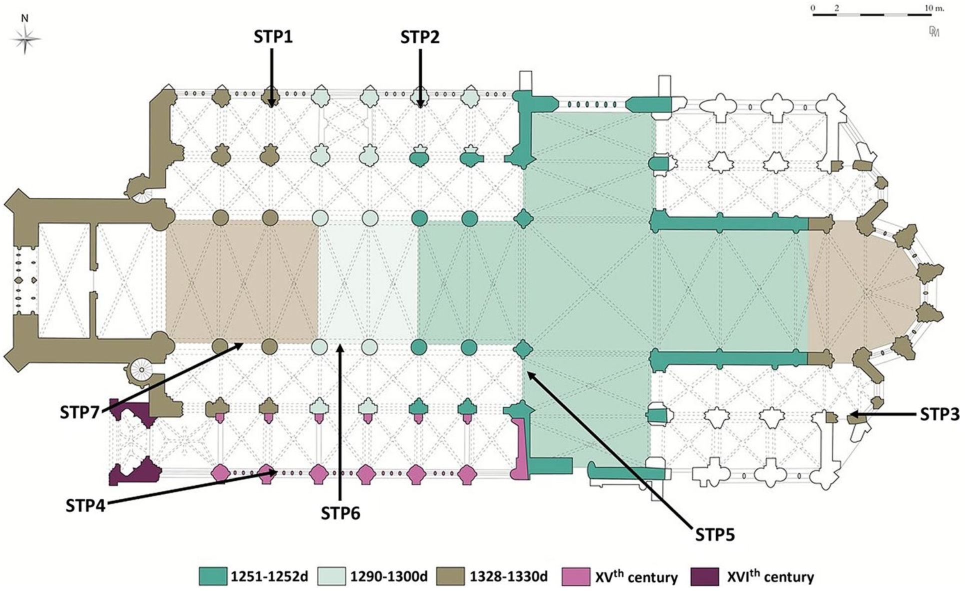


Fig. 4 Location of samples in Saint-Paul cathedral (Liège, Belgium) in relation to building phases (D. Morel and E. Bailleul after Hoffsummer et al. 2005)

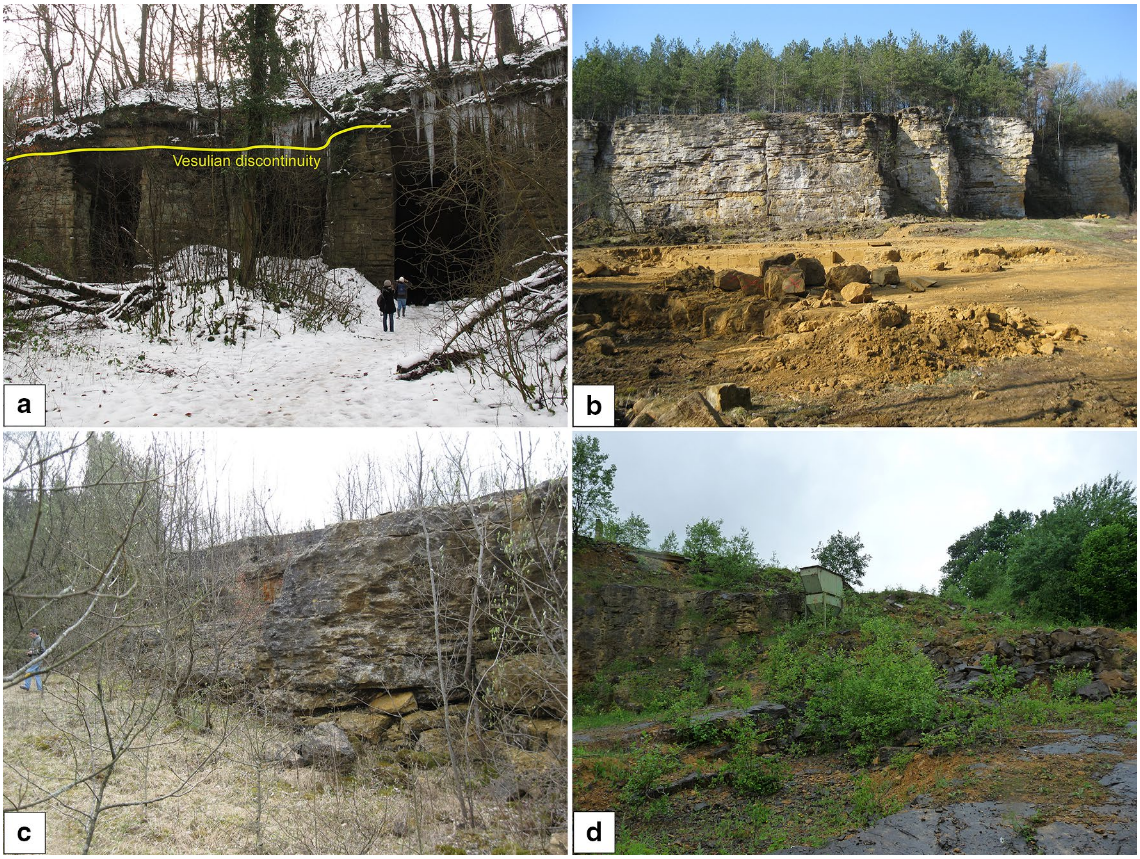


Fig. 5 **a** View of the entrance of the underground quarry of Dom-le-Mesnil (France) with localization of the Vesulian discontinuity, **b** view of the quarry of Hannogne-Saint-Martin (France), **c** view of the Pas-Bayard quarry near Tellancourt (France), view of the quarry of Grandcourt (Belgium)

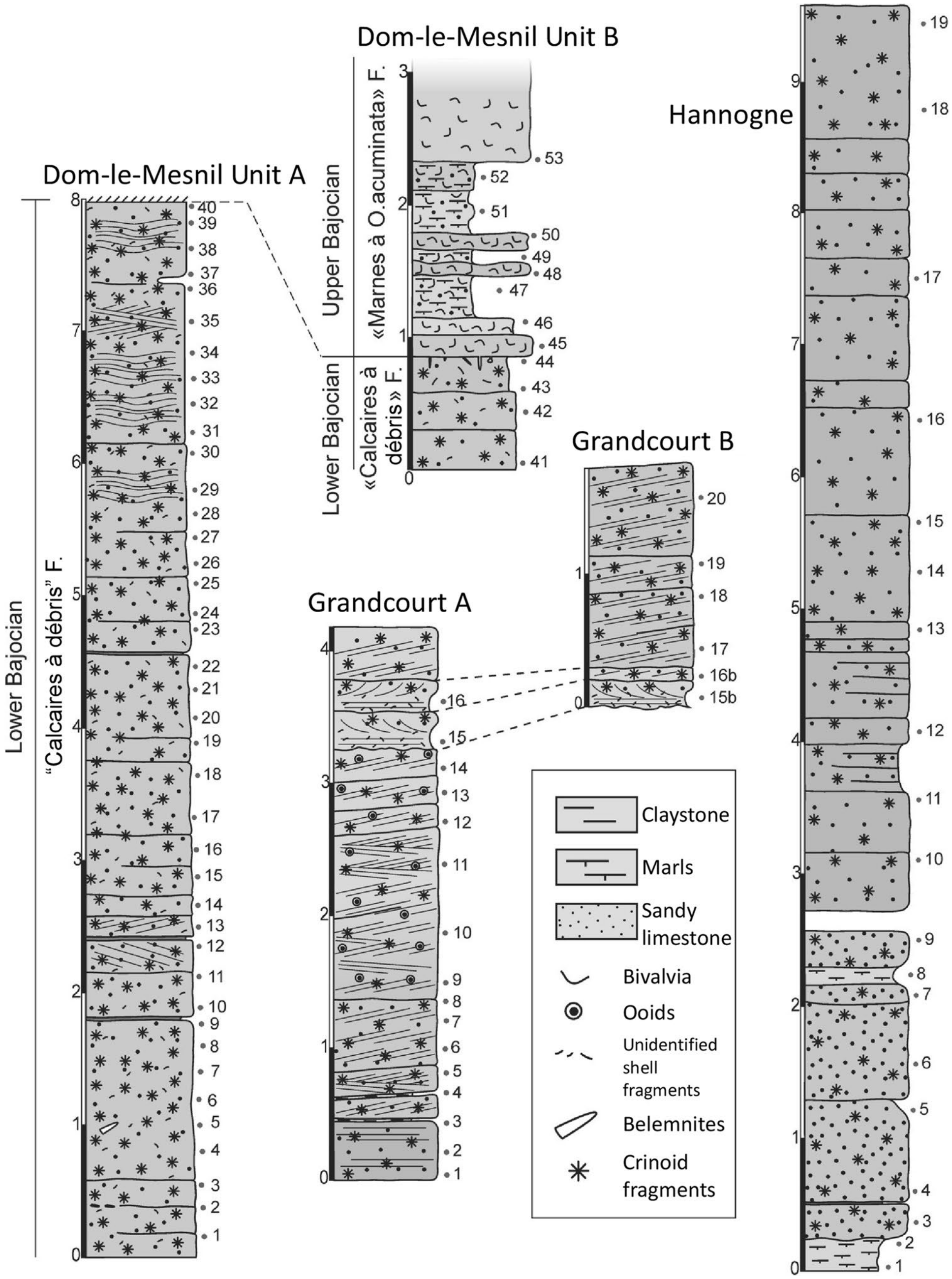


Fig. 6 Geological succession of the quarries of Dom-le-Mesnil, Hannogne-Saint-Martin and Grandcourt

In this area, the quarry is one of the best to obtain pristine samples of Dom stone (Eyssautier-Chuine et al. 2014, 2016). The quarry is about 40 m deep and 30 m wide, and its quarry face is about 10 m high (Fig. 5a). The stone extracted from the quarry is a bioclastic ochre limestone (calcarenite). The lithology is quite homogenous on the whole succession and the stone belongs to the "Calcaires à Débris" Formation dated from Early Bajocian (Mégnien et al. 1980). The lithology is different at the top of the ceiling: it consists in a flagstone of coarse limestone (calcirudite) showing numerous oyster shells. This variation of lithology corresponds to the "Vesulian Discontinuity" which indicates the change from Lower to Upper Bajocian (Brigaud et al. 2009) (Fig. 6, Dom-le-Mesnil B). 53 samples were taken from this quarry, both above and under the "Vesulian Discontinuity".

The quarry of Hannogne-Saint-Martin (N49°40′17″ E4°49′26″) is located south of the village of the same name, 2.5 km to the east of Dom-le-Mesnil. The face of this quarry is about 60 m long and 10 m high (Fig. 5b). It is still quarried at its base, but the major part of the face is covered by vegetation. The extracted stone is the same bioclastic ochre limestone as in Dom-le-Mesnil but here, the Upper Bajocian and the "Vesulian Discontinuity" are lacking. 19 samples were taken in this quarry (Fig. 6).

The quarry of Grandcourt (N49°30′40″ E5°09′56″) is located south of the village of the same name, in the district of Virton (South Belgium, Fig. 5d). This quarry is one of the few Bajocian stone sites from Belgium. It was still in activity during the 1990s and was used for instance for some of the restorations of the Orval Abbey (Thomachot-Schneider et al. 2011), whereas the previous rebuilding phases used the limestone from the Pas-Bayard quarry near Tellancourt (France, Fig. 5c). The stone is a bioclastic and oolithic ochre limestone and it belongs to the Formation of Longwy, Upper Bajocian in age (Belanger 2006). 22 samples were taken in this quarry (Fig. 6).

Results and discussion

Petrographic analyses

All the stones studied are bioclastic, oobioclastic to oolitic grainstones with iron hydroxides. The differences between the samples lay in the size and nature of the bioclasts, the absence/presence and the proportion/size of oolites and quartz grains, and the abundance of iron hydroxides. Three calcitic cements bond the bioclasts: fibrous, syntaxic (around the echinoderms fragments) and blocky-calcite (when the intergranular porosity is fully closed). Lots of the echinoderm fragments are affected by pitting, which reflects a relatively turbulent depositional environment. It was confirmed by the sedimentary figures observed in the various outcrops (Fig. 6).

The samples taken in Dom-le-Mesnil (in the Lower Bajocian formation, inside the underground quarry and in the numerous surroundings open air quarries), Sapogne-et-Feuchères, Hannogne-Saint-Martin and one sample of Pas-Bayard quarry near Tellancourt show only smaller (< 1 mm) bioclasts (Fig. 7a, b), with dominant echinoderm fragments (crinoidal ossicles), small amount of *Ostreidae* shell fragments and foraminifera, very few quartz grains and no oolites as described in Fronteau 2000, Eyssautier-Chuine et al. 2016. The iron hydroxides are present both in the cavities of bioclasts and in the cement bonding the grains. Bioclastic samples from Fagnon (Fig. 7c) and Neuville-les-This are more heterogeneous than in Dom-le-Mesnil area, even if some beds are also dominated by echinoderm fragments.

Some samples collected in Cheveuges, Biermes and Warnécourt (Fig. 7d) contain a significant quantity of quartz grains bonded in calcareous cement, where some bioclasts can be recognized (brachiopods, foraminifera, echinoderms…). One sample taken in Tellancourt shows a notable high content of iron hydroxides.

Several samples contain oolites with other bioclasts (in minor or large amount). This is the case for samples taken in Fagnon, Evigny, Cheveuges, Inor 2, Jaumont and Grandcourt (Fig. 7d–f). One of the samples from Neuville-les-This is even totally oolitic. Among the non-oolitic samples, some of them contain macroscopic bioclasts (> 1 mm), for example, oyster shells. This is the case for samples coming from Rumelange, Inor 1, Pas-Bayard quarry (Fig. 7e), and the upper part of Dom-le-Mesnil quarry, dated from Upper Bajocian.

All the samples taken in Saint-Paul Cathedral are non-oolitic bioclastic grainstones with small bioclasts. Bioclasts are not easily recognizable but are mainly echinoderm fragments. The only differences between samples lay in the content in iron hydroxides and intergranular macroporosity. From a petrographical point of view, the Saint-Paul Cathedral limestones are much more homogeneous than many samples collected in the quarries. All the Cathedral samples are bioclastic grainstones with bioclasts (very small crinoidal ossicles), bonded by a syntaxic cement. No oolitic or shelly limestones were observed in the samples from the cathedral, which excludes numerous potential stone provenances. The facies clearly corresponds to the main soft ochre stone layers collected in the area of Dom-le-Mesnil, Hannogne-Saint-Martin and Feuchères (Fig. 7a, b). One level of Tellancourt also shows this microfacies but its thickness is too small to provide stones as thick as those currently used in the cathedral.

Geochemical analysis

To differentiate the stones of the Cathedral and those from the quarries, some geochemical elements cannot be considered because they were mobilized after the construction of the cathedral. This is the case for chalcophile elements, which have an affinity for sulphur in sulfated crusts, typical of the weathering of limestones in urban environment (e.g. Camuffo et al. 1983; Ausset et al. 1996; Ausset and Lefèvre 2000; Monna et al. 2008).

For the other chemical elements, all the PAAS-normalized REE patterns of samples from Dom-le-Mesnil underground quarry show concave-downward profiles—somewhat depleted when compared to the reference (factor 1.4–4.2)—with a relative enrichment in medium REEs (MREE) and a clear negative Ce anomaly. However, there are some differences between the lower and the upper part of the sedimentary stacking. The limestones sampled in the quarry face above the "Vesulian Discontinuity" (Fig. 8a, Dom-le-Mesnil Unit B) display a relative depletion in REE in comparison with the samples of the lower part of the quarry (Fig. 8a, Dom-le-Mesnil Unit A). This clearly corresponds to the transition from Lower (Unit A) to Upper Bajocian (Unit B) which is also characterized by a change in lithology and the sudden occurrence of many oyster shells. Because of this major change in the limestone and the absence of shelly facies in the cathedral samples, in the following part of this

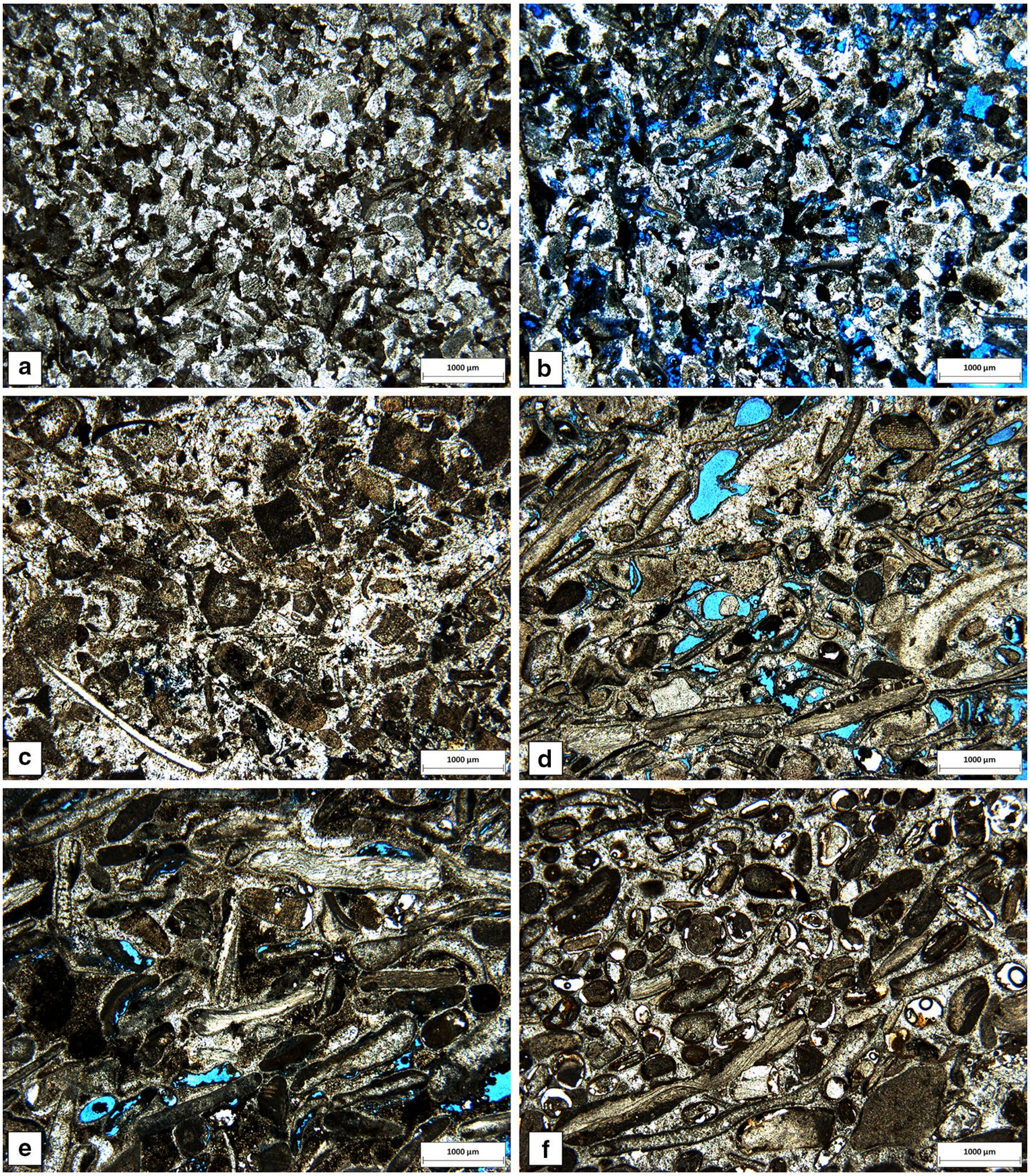


Fig. 7 Petrography of the various studied Bajocian limestones. **a** Dom-le-Mesnil "Calcaires à debris" formation, bioclastic grainstone; **b** Hannogne-Saint-Martin, bioclastic grainstone; **c** Fagnon, bioclastic grainstone; **d** Cheveuges, oobioclastic grainstone with oyster shell fragments and few coarse quartz grains; **e** Pas-Bayard quarry, near Tellancourt (Cons-la-Grandville) oobioclastic grainstone with numerous oyster shell fragments, **f** Jaumont stone from Malancourt-la-Montagne oobioclastic grainstone with oyster shell fragments

manuscript when we refer to the Dom-le-Mesnil quarry, we will only deal with the Dom-le-Mesnil Unit A samples, collected in the "Calcaires à debris" formation from Lower Bajocian. The depletion factor of these samples, with respect to the PAAS reference, ranges between 1.4 and 1.9. Samples from Hannogne-Saint-Martin, dated from Lower Bajocian as Dom-le-Mesnil Unit A, show similar concave-downward REE patterns with a clear negative Ce anomaly, and part of the samples has the same REE content as some samples from Dom-le-Mesnil A (Fig. 8b). This clear overlapping of the geochemical REE imprints, makes any attempt to discriminate the two quarries impossible.

The samples of the quarry of Grandcourt display PAAS-normalized REE patterns slightly different from those of Dom-le-Mesnil and Hannogne (Fig. 9) because (1) they present a weaker negative Ce anomaly ($0.66 < \mathrm{Ce/Ce^*} <$

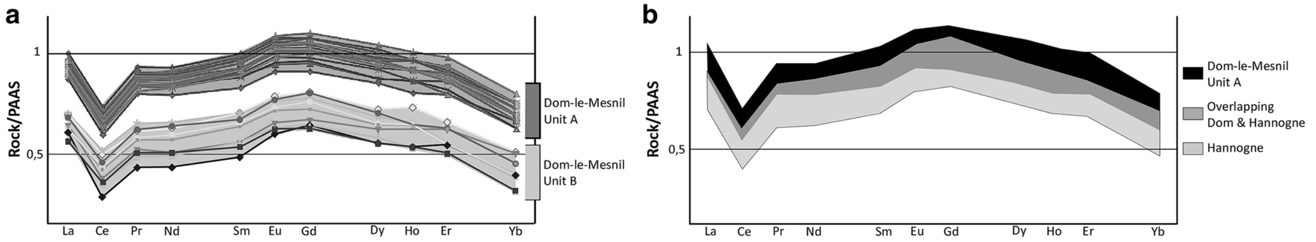


Fig. 8 a Comparison between Dom-le-Mesnil quarry Unit A Lower Bajocian, Unit B Upper Bajocian. PAAS-normalized REE profiles b Comparison between Dom-le-Mesnil Unit A Lower Bajocian and Hannogne-Saint-Martin Lower Bajocian. PAAS-normalized REE profiles

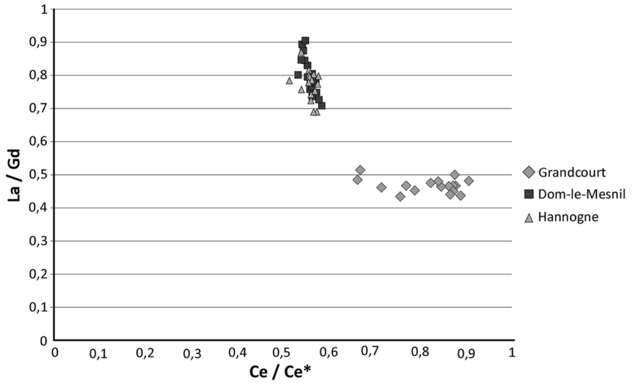


Fig. 9 Enrichment in MREE and Ce anomaly in Dom-le-Mesnil, Hannogne-Saint-Martin and Grandcourt samples

0.90 in Grandcourt and 0.51 < Ce/Ce* < 0.59 in Hannogne and Dom-le-Mesnil Unit A) and (2) they are relatively more enriched in MREE (0.43 < La/Gd < 0.51 in Grandcourt and 0.69 < La/Gd < 0.90 in Hannogne and Dom-le-Mesnil Unit A).

One of Bajocian samples collected in an ancient quarry of Sapogne-et-Feuchères (Fig. 10) shows a similar REE pattern to those of Dom-le-Mesnil Unit A and Hannogne-Saint-Martin (Fig. 11). All other samples differ to a greater or lesser extent from the former samples. They display a similar concave-downward REE profile, but the stones from Fagnon, Evigny, Warnécourt, Rumelange, Neuville-les-This and the base of Pas Bayard Quarry near Tellancourt are relatively depleted in REE (factor 3.8 to 15.9 in comparison with the PAAS reference). Those from Jaumont

Fig. 10 Comparison between other Bajocian stones. PAAS-normalized REE profiles

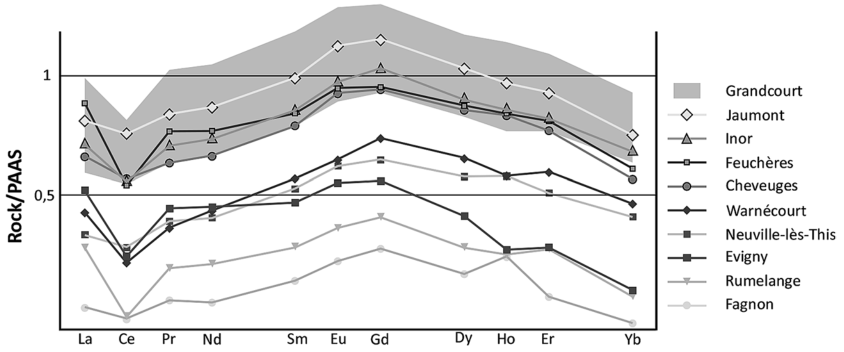
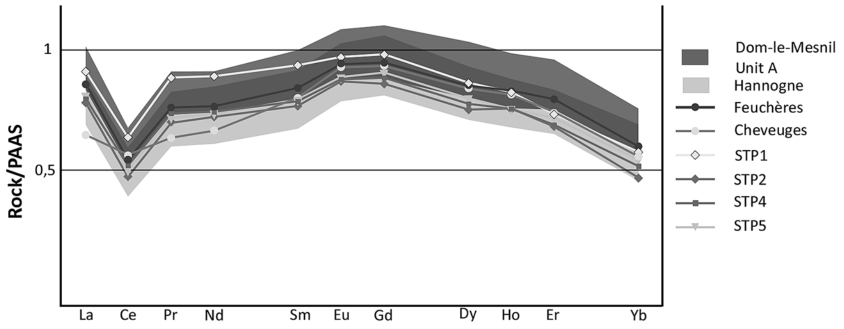


Fig. 11 REE normalization: comparison between St Paul samples and some Bajocian quarries



(Malancourt-la-Montagne) and Cheveuges show a smaller negative Ce anomaly. The latter two samples, Inor 2 and Sapogne-et-Feuchères have a pattern similar to the Grandcourt stone.

Accordingly, all the PAAS-normalized REE patterns of Bajocian samples display a clear negative Ce anomaly. This anomaly is typical of oxidizing marine environments. In such environment, Ce(III) is oxidized to Ce(IV), which is subject to preferential scavenging over REE(III)s (Alibo and Nozaki 1999; Dia et al. 2000). The intensity of this anomaly somewhat varies from one sample to another and allows to discriminate stones which otherwise display ***similar REE profiles (e.g. Grandcourt vs Dom-le-Mesnil Unit A). This difference of Ce anomaly intensity could be due to the presence of Fe-oxyhydroxides associated to the oxidation of Ce(III) (Davranche et al. 2004). Moreover, the capacity for Ce(III) oxidation is higher in systems in which fresh Fe-oxyhydroxides precipitate than in systems in which dissolved Ce interacts with preformed Fe-oxyhydroxides (Bau 1999).

St Paul cathedral samples show a concave-downward profile with a clear negative Ce anomaly and a relative enrichment in MREE. The Ce/Ce* value for St Paul samples ranges from 0.55 to 0.62. The depletion factor, compared to the PAAS reference, ranges from 1.5 to 2.1 (1.3 for STP6). The comparison between results from quarries and St Paul cathedral displays that samples have a similar PAAS-normalized REE pattern (Fig. 11), except for the sample STP6 which is relatively enriched in MREE. Specifically, the samples taken in the cathedral reveal a REE pattern perfectly similar to the REE pattern of the stones of Dom-le-Mesnil Unit A, Hannogne and Feuchères. The other Bajocian stones have quite different REE patterns, containing less REE (e.g. Evigny), or because their negative Ce anomaly is much lower (e.g. Cheveuges) (Fig. 11).

Conclusions

Geochemical and petrographical analyses have been performed to identify the origin of the stones used in Saint-Paul Cathedral (Liège, Belgium). Both methods allow us to point out an area with at least three ancient quarries (Dom-le-Mesnil, Hannogne and Feuchères) in which the stones present the same petrographical and geochemical characteristics as those of the Saint-Paul Cathedral. These quarries are close to each other and they are located at less than 10 km from the ancient ports of Donchery and Mezières, on the Meuse River. We highlight a geographical area of about 5 km^2 which is most likely the origin of the previously called "Lorraine limestones" used in Saint-Paul Cathedral. This conclusion is in agreement with the historical sources which testified trade relationship between Liège and the port of Donchery, but did not clearly precise the quarry location.

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