Diagenesis of Luxembourg Sandstone

by

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Abstract

Research has been conducted into the diagenesis of the Luxembourg Sandstone. Literature studies were followed by a visit to the outcrop, after which thin sections were studied. The Luxembourg Sandstone Formation has been deposited in the Hettangian and Sinemurian, both lower Jurassic ages. A sea strait connecting the Northern German Basin and the Paris Basin was located in present day Luxembourg. A tidal dominated delta deposited the weathering products form a part of the Rheno-hercynian Zone, the Ardennes, into the transgressive sea strait to create sandstone deposits. The outcrop near the village of Echternach is characterised by two rock types visible as horizontal beds and lenses: one well cemented and a less cemented sandstone. The less cemented zones tend to be better resistant to weathering and this causes the less cemented rock to overhang the cemented rock. The cemented zones have been cemented with calcite crystals and minor amounts of quartz cement. The sandstone consist of fine grained, moderately sorted, angular quartz grains with minor amounts of feldspars, opaque minerals, muscovite and zircon crystals. Detrital mudstone grains and ferroan cement were also present. The cemented rocks are classified as Lithic Arenites whilst the less cemented zones are classified as Sublithic Arenite, both have a recycled orogenic provenance. Three parameters have influenced the cementation. Firstly permeability differences caused by deposition of clay and deposition of coarser material. Paths of permeability have formed through the sediments and this favoured cementation. Secondly, heterogeneous deposition of carbonate holding content provided extra nucleation sites, again encouraging cementation. Lastly, carbonate redistribution took place in later stages causing carbonates to move from less cemented zones to cemented zones, causing even more cement to precipitate. Since calcite crystals dissolve more easily than quartz in the meteoric realm, the cemented rocks have been dissolved more, creating the appearance of the formation.

Contents

1
Introduction

During the first years excursion, many outcrops in Luxembourg, Belgium and Germany are visited. When visiting the area of Echternach in Luxembourg a large sandstone outcrop is passed, the Luxembourg Sandstone. Steep steps allow you reach the large sandstone outcrop. At this moment the Liassic Sandstone is clearly visible. When looking closer at it, the difference in weathering becomes obvious. Some parts look intact whilst other parts show deep scars, both thin and thick beds look weathered. Two different rocks are visible, one grey and the other more yellow, the yellow rocks look better resistant to weathering than the grey rocks. When continuing the walk Northwestward, away from Echternach, the same feature are visible. What is the reason some areas of the sandstone look very weathered and other parts are not. This thesis will deal with this question. The geological history will be consulted to find out more about the depositional environment of the sandstone. Macroscopic and microscopic research should lead to an explanation as to why the rocks show such different weathering.

Figure 1.1: Outcrop of the Luxembourg Sandstone near Echternach

2
Methodology

To find answers to the questions in this bachelor thesis, different ways of research will be implemented. The first step taken was to find out more about the geological setting of the area. By going over geological maps of the area, a first image of the formation will be created. The geological history of the Ardennes and the Eifel was used to get a better understanding of the deposition. The formation of nearby basins and oceans was used as well to gain more knowledge about the Luxembourg Sandstone. Literature was consulted and a few articles proved useful; these articles formed a guideline through the history and also the diagenesis of the formation. Even though a few samples were available for the macroscopic research, a trip to the outcrop in Luxembourg was necessary. Some useful pictures were taken and this helped to understand the questions better. Visiting the outcrop also helped to understand what was written in literature. Some extra samples were taken from the outcrop.

The different features of the outcrop were measured and notable characteristics were noted and photographed. Samples were described using hand lenses and the differences between the different rocks already became clear. To gather more information about the rocks, thin sections were prepared. Multiple samples were taken from both rock types. One sample of the grey rock and one sample of the yellow rock were taken to the laboratory. These rocks were cut into smaller pieces, labelled and impregnated. Impregnation was necessary as the rocks were too soft for the later grinding process. The impregnated rocks were glued to a glass plate and cut at 1mm. The leftovers are photographed and visible in figure 5.1. Afterwards, the thin sections were ground until the inference colours of quartz were correct, a thickness of 30µm was desired. In the end, two sections of each sample were made. These were covered with a glass plate and glued with Canada Balsem. The thin sections were labelled L11 and L12 for the slow weathering rock, and S11 and S12 for fast weathering rock samples.

The thin sections were analysed using a Leica DM LM microscope. Most of the time crossed polars were used, occasionally the analyser was taken out to look into the borders of the grains. The samples were analysed one at the time. The mineral content, sorting, grain sizes and special features were noted. Special attention was put into the cementation of the samples and which minerals were still intact and which were altered. This would help the further analyses of the samples. Point counting was initially planned, but the content was measured percentage wise. Comparison figures were used to estimate the mineral content. The percentages were plotted in a ternary diagram using Excel. The values for QFL were summed and were slightly adapted if 100 percent was not reached. Since the values were estimated, this caused no problems regarding the significance. The obtained percentages were converted into coordinates to be plotted inside the ternary diagram. The percentages were plotted in the Dickinson figure to find the provenance of the sandstone. Pettijohn classification with quartz, feldspars, lithics and matrix percentage was used to classify and name the sandstone. The data was plotted in a 1 dimensional diagram, not in the 3 dimensional Pettijohn diagram. The ternary diagram with data was then projected to the right matrix content to find the name.

Images of the samples were taken using the Leica MC120 HD Microscope Camera and were processed on the computer using the Leica Application suite. Four different amplifications were available on the microscope: 4x, 10x, 20x and 50x. The correct scales were available in the programme and have been added in all pictures in this thesis.

The diagenetic history of the samples was looked into. Which events occurred before which events, this could help to explain why the outcrop looks the way it does now. This in combination with the geological history, the features of the outcrop and the knowledge about sedimentology will lead to an outcome of the research. The diagenesis will be described and the answer will be given as to why the we see such different weathering patterns. A few options will be named as to how the deposition has lead to the different weathering patterns.

3
Geological History

The geological history of Luxembourg is important to be able to answer the question as to why the Luxembourg Sandstone shows different types of weathering. Map 3.1 below shows the current geology of Luxembourg.

The Luxembourg sandstone has been deposited (Colbach, 2005)in the Hettangian and the Sinemurian stages, both lower Jurassic. They span from 201.3 Ma - 199.3 Ma and 199.3 Ma - 190.8 Ma respectively (Walker *et al.*, 2012). However, to explain the sedimentological processes better, it is necessary to go back in time further. The Ardennes, the Northern German Basin, the Eifel depression and the Paris Basin will be discussed as they play an important role in the deposition of formation.

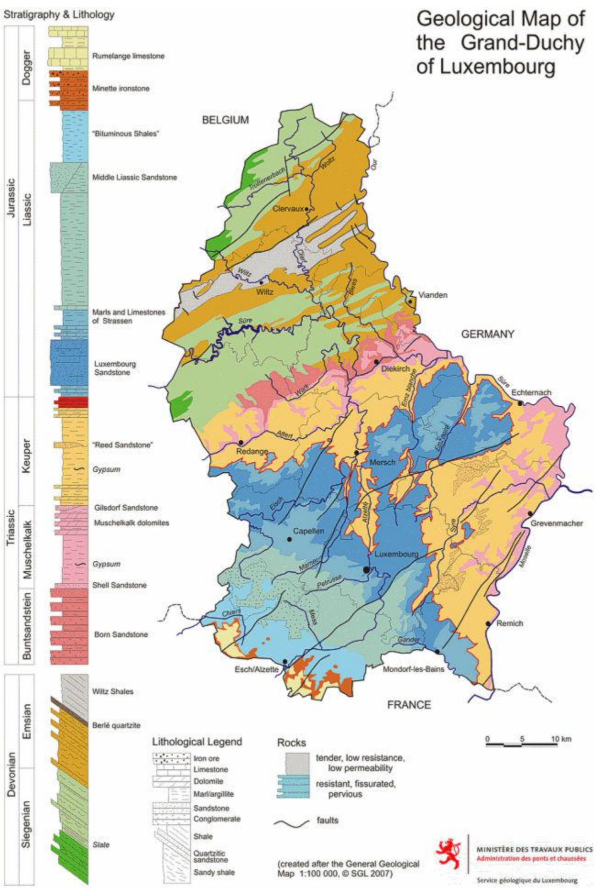


Figure 3.1: Geological map of Luxembourg. From :Maquil and Colbach, 2009

3.1. The Ardennes

The Hercynian Orogeny took place between around 390 Ma and 300 Ma, but the main events took place at the end of the Carboniferous, 300 Ma. Tectonic forces moved Gondwana north and it crashed into Laurasia to form the super continent Pangea (Blom, 2016). An important result of this orogeny is the Rhenohercynian Zone, which the Ardennes are a part of. The following paragraph describes the formation of this zone.

The Hercynian Basin was created by extension in the Early Devonian. During the middle Devonian, the oceanic plate of the Rheic Ocean subducted under Euramerica and caused the Rhenohercynian basin to form a Back Arc basin (Ziegler, 1990). The collision of Gondwana and Laurasia during the Hercynian Orogeny caused the Devonian and early Carboniferous sediments in the Rhenohercynian Basin to slide over the foreland as Piggyback Basins (Franke, 1989). During later stages the Rhenohercynian zone was further folded and it subsided due to the rapid rise of the Hercynian Mountains. The erosion products form these mountains filled the basin and caused it to emerge above sea level.

3.2. North German Basin

The North German Basin is a part of the much larger South Permian Basin. The foreland of the Hercynian Mountains is the area of the formation of the North German Basin. The collapse of the Hercynian Mountains caused the foreland to subside. This in combination with magmatic activity and thermal thinning of the crust in response to final stages of the unification of Pangea, caused the first subsidence of the area. (Doornenbal and Stevenson, 2010) The basin was rapidly filled with sediments and this accumulation caused further subsidence (Glennie, 1995). The Arctic North-Atlantic rift system propagated into the South Permian Basin due to the break up of Pangea during the Triassic and caused further subsidence in the North German Basin.

The Basin had been connected to the Paleo-Tethys Ocean during the Permian. This meant different sediments could accumulate in a marine environment. The sandstones of the Rotliegendes are an example and later during the Triassic, eolian deposits can be found due to the arid environment at that time.

3.3. Paris Basin

The Hercynian Orogeny not only created the Ardennes, it transformed large parts of Europe into a mountain range. Present-day France was also pushed up during the orogeny. The area of the Paris Basin was now a plateau in between several large mountain ranges (Balusseau, 1981). The Vosges to the East, the Armorican Massif to the West, the Massif Central to the South and the Rhenohercynian Mountains to the North East (Woudloper, 2008). Post-orogenic processes caused the plateau to sink. The erosion of the above-mentioned mountains and the sedimentation of the these products continued into the Triassic. During the late Triassic the basin was connected with the North German Basin, a sea which covered large parts of Germany, the Netherlands and Poland.

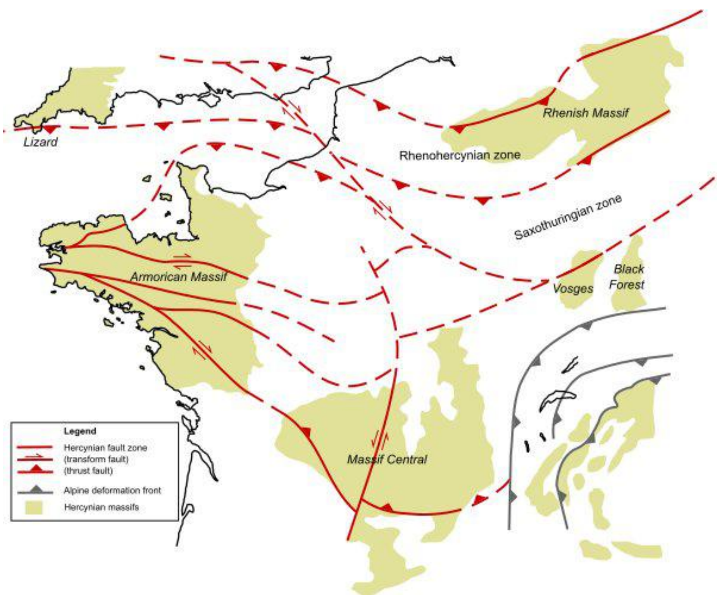


Figure 3.2: Location of the various mountain ranges. The Paris Basin was located in the middle of them. From: Woudloper, 2008

The water in the North German Basin could get into the Paris Basin by passing through the Eifel Depression. This depression was located in between the Ardennes and the Eifel, the lower area formed a channel through which the Paris Basin could be filled (van den Brill and Swennen, 2008). The depression can be seen in figure 3.3. Apart from this input of sediments, the other mountain ranges which are mentioned above also provided sediments which filled up the Paris Basin. During the late Jurassic, when Pangea started to fall apart, the Paris Basin was connected with the Aquitaine Basin which was located south-west of the Paris Basin. The basin further subsided and the deposition environment became deep marine. The importance of the Paris Basin for the Luxembourg Sandstone ends here and the further events of this basin will not be discussed.

3.4. The Eifel Depression

The basement of the Eifel Depression is made up of a fold-and-thrust belt consisting of Devonian rocks. This fold-and-thrust belt was created by the Hercynian Orogeny and is located in the Rhenohercynian zone. The Eifel Depression continues into the Luxembough-Trier Basin (Schintgen and Forster, 2013).

At the end of the Permian, the Northern German Basin had been, as stated before, connected with the Paleo-Tethys Ocean. At the border between the Northern German basin and the Eifel depression,

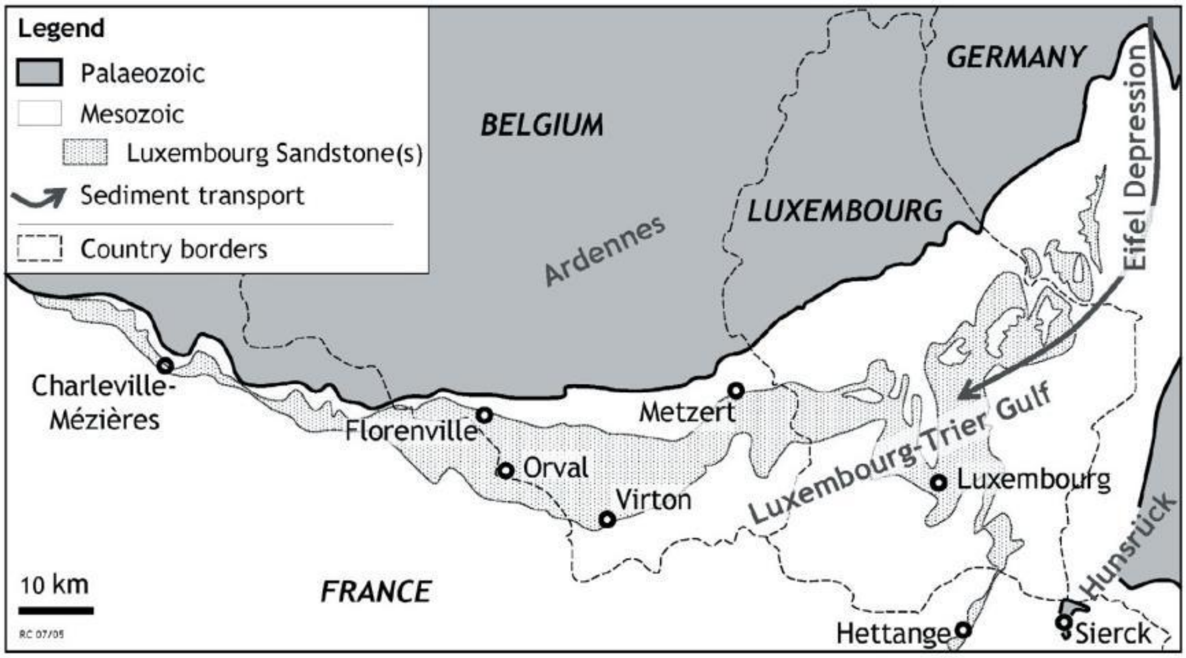


Figure 3.3: The Eifel Depression. From:Colbach, 2005

sandstones and alluvial fans containing also conglomerates from the Buntsandstein are present. This meant that already during the lower Triassic, an elevation difference was present between the two areas. First rivers connected the two area, later the rivers joined and became a sea strait. Limestones from Muschelkalk are also present and this emphasises the statement of a shallow sea in the Eifel depression during the middle Triassic. Outcrops of these Muschelkalk limestones can be found in the vicinity of Echternach. Regression during the Keuper caused evaporitic and clastic deposits to occur. Transgression occurred during the late Keuper, which caused marine deposits again (Schintgen and Forster, 2013). This transgression continued into the Jurassic and thus from this period onwards the Eifel depression has been submerged by a sea and this eventually caused the deposition of the Luxembourg Sandstone.

3.5. Deposition of Luxembourg Sandstone

The Northern German Sea, The Paris Basin and the Eifel depression form the three main features which caused the Luxembourg Sandstone to form. We will now look deeper into the deposition of the Sandstone.
As figure 3.3 shows, the Luxembourg Sandstone was deposited in an area were a sea interacts with higher ground, a littoral zone with the higher ground being the Ardennes in this case. The rivers transported the sediments from the Ardennes and deposited these if the velocity, and thus the energy, of the river was too low to hold the sediments in suspension, into the sea (Mertens *et al.*, Berners, 1983, 1983).
The deposition of the Luxembourg Sandstone has been studied well and an article of Schintgen and Forster (12) shows the thickness of the formation throughout Luxembourg and its surroundings. The littoral deposition of the Luxembourg Sandstone can be emphasised using figure 3.4. The figure shows well the shape as well the NE-SW trend of the Eifel depression as was already shown in figure 3.3. Moving further towards the SE the thickness of the formation diminishes until there is none left. At these locations the Eifel Depression was deeper and this resulted in more marly and bioclastic depositions instead of the coarser Luxembourg Sandstones (Schintgen and Forster, 2013).

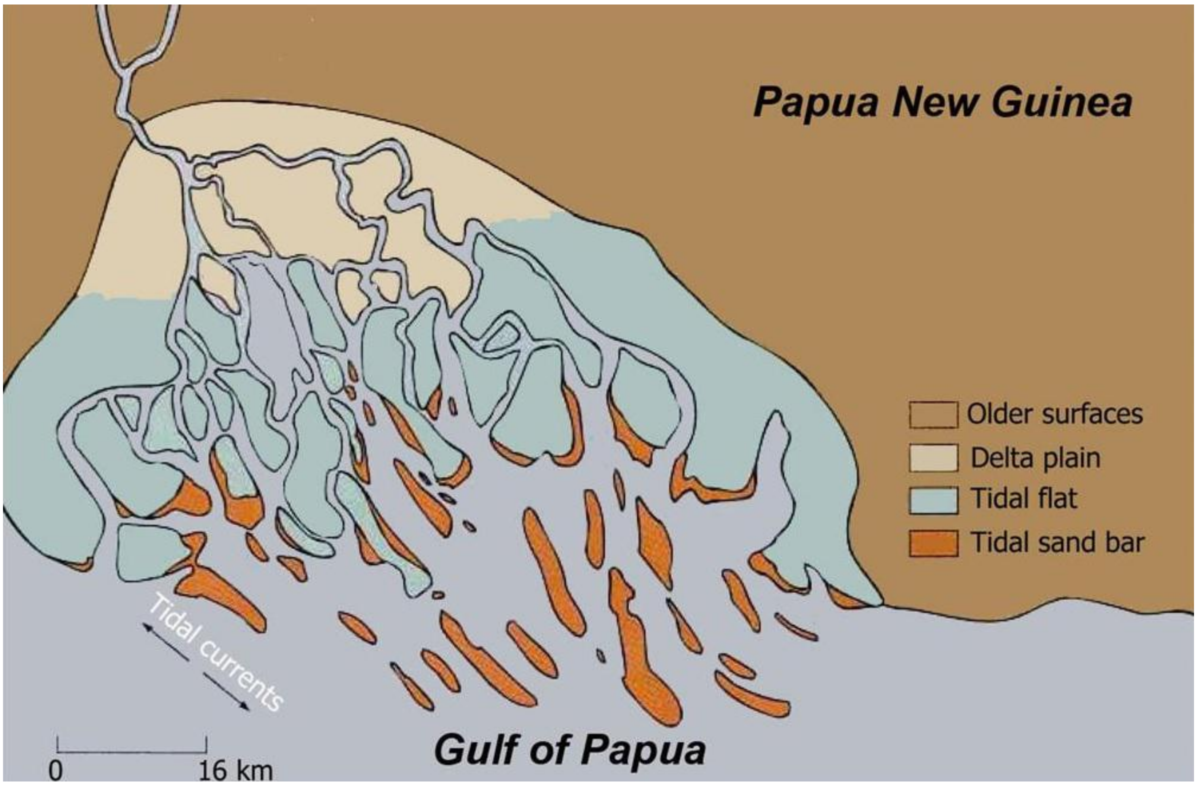


Figure 3.5: A tide dominated delta. From: Boyd, 2007

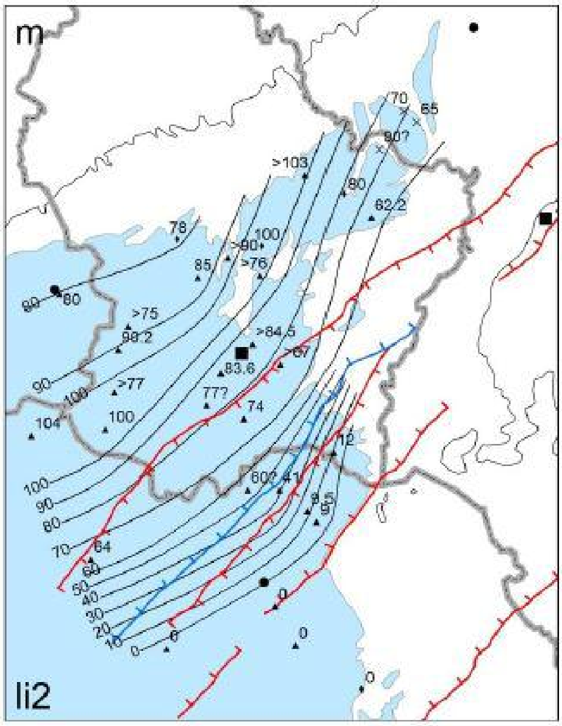


Figure 3.4: Isopachs of the Luxembourg Sandstone. From: Schintgen and Forster, 2013

Since the Eifel Depression was connected to the North German Basin and the Paris Basin, which were also connected to the Tethys Ocean, the sea experienced tides. The Tethys Ocean can be seen in the lower right of figure 3.6. The Tethys Ocean is also called the Neo-Tethys Ocean, as is done in figure 3.6, this is however not the same as the Paleo-Tethys Ocean. The delta in this case was a tidal dominated delta (van den Brill and Swennen, Mertens *et al.*, 2008, 1983). The tides will affect the delta, especially the delta front will be altered. Given the location of the Eifel depression the area experiences a meso-tidal environment (Mertens *et al.*, 1983).

Figure 3.5 shows the Gulf of Papua and is a good example of a tidal dominated delta. Due to the incoming and leaving tides the sand will not have enough time to deposit in a regular delta shape. The delta front will not grow into the sea as a triangle form, but it will create sand bars perpendicular to the coast. This figure is solely used to illustrate the shape of a tidal dominated delta, in this case the Gulf of Papua. It is unsure whether the Luxembourg Sandstone was deposited as this figure illustrates.

The Luxembourg Sandstone can be found throughout Luxembourg. Berners (14) found that the oldest Luxembourg Sandstones are found in the east of Luxembourg. The dating of the sandstones was done by looking at the ammonites which are present. Some ammonites only lived at certain times and this proved the youngest rocks were in the west of Luxembourg. This westward movement of the sandstone can be explained by the sea level change during the Jurassic. The eustatic sea level drastically dropped during the Triassic but rose again from the Jurassic onwards and this rise can be seen in the Luxembourg Sandstone. The transgressive sea moved up onto the Ardennes and shifted the deposition area land inward. At the border of Hettangian and Sinemurian a peak transgression has occurred (van den Brill and Swennen, 2008). This moved the depocentre even more onto the Ardennes.

The climate during the Jurassic was warm and humid, a tropic climate. This climate will cause rocks to weather faster and the sedimentation rate will be high. A tropic climate will also cause iron to oxidise but it is unsure whether iron is present in the Luxembourg Sandstone. What is certain is that Toarcian and Aalenian (early and middle Jurassic ages (Walker *et al.*, 2012)) deposits contain iron parts coming from the weathering of the Hercynian Mountains. These iron minerals precipitated and formed ooids (van Tooren, 2015). The Luxembourg Sandstone is deposited earlier than these iron minerals, but the weathering from the Hercynian Mountains is also the origin of the Luxembourg Sandstone. This means that iron could be present in the formation.

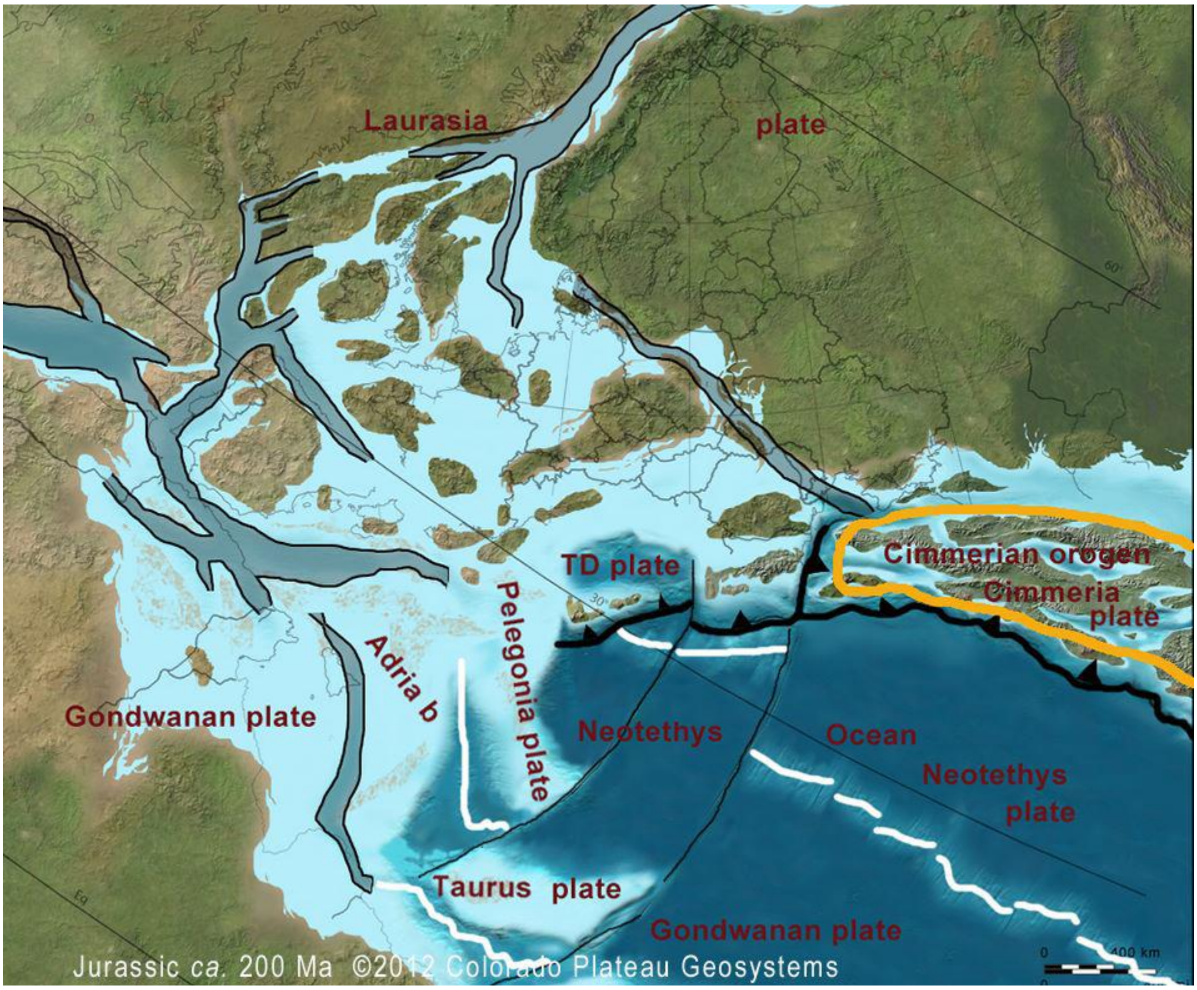


Figure 3.6: Europe during Jurassic Ca. 200 Ma. From:Colorado Plateau Geosystems, 2012

The Luxembourg Sandstone remained buried until the middle Cenozoicum. Uplift occurred during the Pliocene due to Alpine orogony (Blom, 2016). This caused the Luxembourg Sandstone to rise and was now exposed to weathering form the elements.

4

Description of outcrop

The large sandstones outcrops can be visited after a short walk when visiting the area between Echternach and Berdorf. What strikes most is the big difference between the rocks. When walking in North-eastern direction the outcrops look different every 20 meters. This chapter will deal with the description of the outcrop as shown in figs. 4.1 and 4.2. These areas showed the difference between the two rocks and the weathering the best.

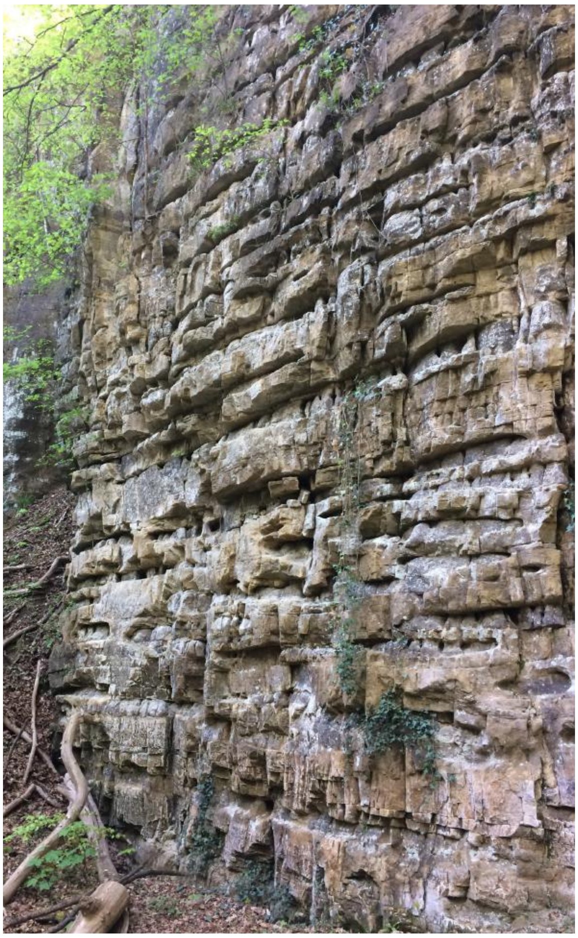


Figure 4.1: Outcrop of Luxembourg Sandstone.

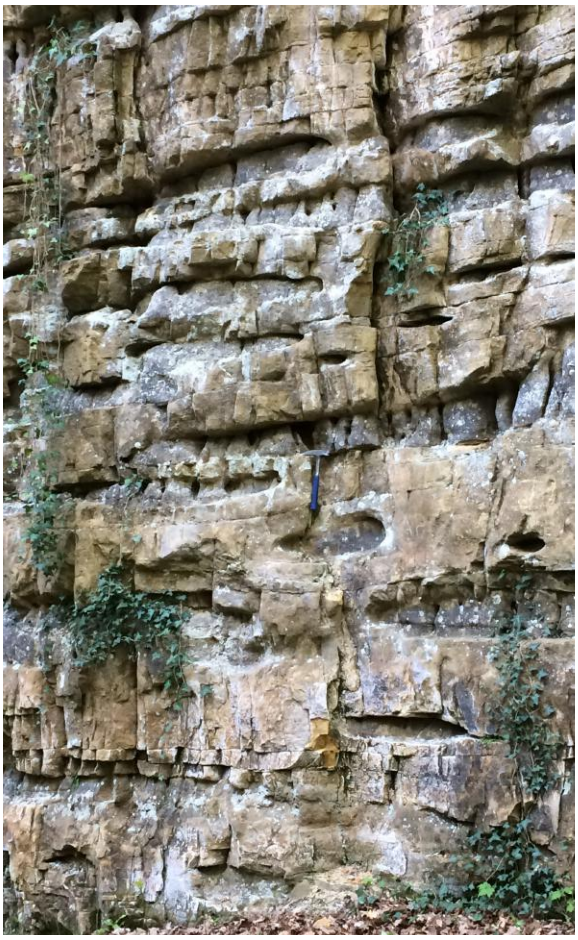


Figure 4.2: Thickness of the two rocks types.

Two different kind of rocks can be distinguished quickly. The yellow thicker beds and the grey whitish, less thick parts. From a distance it looks like the two rocks are alternating rhythmically but from closer by the irregular alternations are clearly visible. The yellowish beds seem stronger as they stick out whilst the grey rock has disappeared into the outcrop. The thickness of the layers of the yellow rock vary from around 15-60 cm. The layers of the grey rock are less thick and measure around 10-30cm. The dimensions of the rocks are visible in figure 4.2. Both rocks have been weathered. The yellow rock

Figure 4.3: Sharp Border between grey and yellow rock

Figure 4.4: Lenses of the grey rock within the Luxembourg Sandstone formation.

shows whiter spots and darker areas and vegetation is present. The rock shows small vertical joints of centimetre scale to around 10 cm. Larger horizontal layers can be distinguished as well, the horizontal layers are around 5-15 cm thick and continue horizontally for multiple meters. The rock shows sharp edges. The border between the yellow and the grey rock is sharp, this is shown in figure 4.3.

The grey rock shows a stronger weathering pattern than the yellow rock. Deep vertical joints are visible. They extend throughout the thickness of the layer or lens. The width of these joints varies from a centimetre to wider gaps of around 5cm. The dimensions of the gaps in the grey rock are well visible in figure 4.2.

What strikes are the lenses made up of the grey rock. The relief of the outcrop shows the grey beds and lenses retracted into the outcrop while the yellow rocks do stand out. The thickness and width of the lenses varies strongly. Figure 4.4 shows some lenses which are about 5cm in height and 35cm in width. At the top of figure 4.4 thicker beds of the grey rock, and a thick yellow rock bed are visible. These beds are not so much lensoid, but look more like regular horizontal beds. The outcrop shows a combination of lenses with variable thicknesses and horizontal beds. Figure 4.5 indicates this. The lenses have been indicated with red ellipses, the horizontal beds are pointed out with yellow lines. More features are visible in the figure but have not been indicated.

4.1. Samples

The difference between the two rocks becomes even more clear when taking a sample of both. The yellow rock shows a typical sandstone exterior. It is quite soft and can be scratched with a fingernail. The grains can be seen with the naked eye and the shiny quartz shows up clearly. The empty pores in between the grains are clearly present. When the pieces are cut in two to prepare for the thin sections, some brown veins can be seen in the yellow rock. This might be rust or brownish clay.
The grey rock has a different appearance. It is more grey whitish, and is not as porous as the yellow rock and feels heavier. It cannot be scratched with a fingernail. The grains are more difficult to see but they are still visible. The piece of rock was also harder to take from the outcrop.

The grey rock is much harder than the yellow one, however, in the outcrop the grey rock seems to be weathered more. The yellow, softer rock overhangs the harder grey rock. This doesn't sound logic at all. How is it possible that a softer rock is better resistant to weathering? The answer has to lie in chemical weathering. To find out more about this, thin sections should be used. The mineralogical composition of the two rocks could help to find an answer as to why the grey rock experiences heavier weathering. The microscopical research will be discussed in chapter 5.

Figure 4.5: Lenses and horizontal beds of the grey rock at the outcrop. Horizontal beds and lenses of the grey rocks are indicated with yellow lines and red ellipses respectively.

5
Microscopical characteristics

The geological history did not provide enough information to explain the different weathering patterns of the two rocks. Visiting the outcrop did clarify some matter and gave an overview of the area. However, microscopical research is needed to further investigate the different rocks. Their mineralogy could lead to an answer as to why the two rocks are so different. This chapter will deal with this part of the research.

Figure 5.1: The four impregnated samples from which the sections were created

5.1. Analysis of thin sections

Thin sections L11 & L12 are created from the yellow rock, sections S11 & S12 from the grey rock. The sections from the two samples are very different, the images can be found in Appendices A and B. Figure A.1a and figure B.1a show that the two samples not only differ macroscopic, but that they are also very different in the microscopic scale.

The analyses will start with a general description of the thin sections and the mineral content. The analysis of the diagenetic processes and classification of the samples will be done further into this chapter.

5.1.1. Thin sections S11 & S12

The sample consists of very fine to fine quartz grains which are moderately sorted and show angular shapes. Quartz is the main mineral and lots of calcite crystals are present. Almost no porosity is left as the pores have been cemented with calcite crystals. The high interference colours indicate calcite crystals and are well visible in between the quartz grains in figure A.1c. The shape of the calcite crystals in the pores is blocky. Drusy crystals could not be found using this microscope. On some quartz grains corrosive calcite is found: the quartz is corroded by the alkaline pore fluids and the calcite crystals have precipitated into these areas; calcite crystals have replaced a part of the quartz grains. Figure A.1c shows well the corrosive calcite cement onto a quartz grain. Corrosive calcite cement can be seen often throughout the samples S11 and S12. The same figure also shows the different quartz grains. The grain in the middle is different from the grains around it: the middle grain is a polycrystalline quartz, whilst the outer grains are monocrystalline grains.

Deformed quartz crystals are also found. These crystals look similar to polycrystalline quartz crystals but show lammelae. Syntaxial overgrowth is present on some of these monocrystalline grains, quartz cement has grown around the quartz grains in such a way that it is optically identical to the quartz grain. Quartz cement is precipitated in this way, around existing quartz grains. Overgrowth is well visible in figure A.1d.
The contacts between the grains include concave-convex contacts, long contacts between grains and sutured grains, the latter is shown in figure A.1e.
Throughout these samples, brown rounded grains can be found. When looking at it with a large magnification, the high interference colours of calcite are visible. These grains can be classified as limestone grains, see figure A.1f. Some fossils or remnants of animals are visible in the samples. The fossils will dissolve and the newly formed pore will fill with cement. The shape of the original fossil is still visible. Figure A.1b visualises this and show the probable remnants of an Echinoderm. Lots of fossils are found in the thin sections.
Throughout the samples, opaque minerals are visible. These could be pyrite crystals, but this cannot be confirmed. Pyrite does occur in sedimentary rocks. For this thesis, they are described as opaque minerals.
Some small very fine crystalline glauconite grains are present in the thin sections. A single zircon grain is also found.

5.1.2. Thin sections L11 & L12

The samples consist of very fine to fine, moderately sorted, angular shaped quartz grains. Quartz is the dominant mineral in these sections, but other minerals are also present. The black areas with small spots visible on the sections are empty pores (figure B.1a) and since lots of these are present, the porosity is relatively high. The brown bands through the samples are well visible in the sections and are identified as ferroan cement (figure B.1b). Ferroan cement is present throughout the sample in small amounts. The figure indicates the ferroan cement content on of the bands where the amount of iron is much higher.

These samples do not contain much calcite cement and the pores remain empty in most cases. The grains seem to be close together and more grain contacts are visible. The grain contacts consist of sutured grains, long contacts and some concave-convex contacts. The dusty rim between the two grain contacts can be clearly seen in figure B.1c.
No fossils were found in these samples. Apart from quartz grains, both mono- and polycrystalline, these samples also contain different minerals. Muscovite (B.1d), Feldspars (Microcline) (B.1f) and chert are found. Deformed quartz is, just like the in the grey samples, found (figure B.1e). Deformed quartz's have a detrital origin. The Hercynian Orogeny will have caused older rocks with quartz grains to deform and these were stored in the Ardennes after which they were eroded and transported into the delta where they were deposited (figure B.1e).
Quartz, feldspar and lithic content for all four thin sections were estimated and can be found in table 5.1.

5.1.3. Differences

The main difference between the two sample sets is the calcite cement. The grey rock samples show all the pores filled with calcite cement and almost no porosity left. The yellow rock samples show a higher porosity, some ferroan cement is present though but most pores are empty. The porosity of the yellow rock had already been estimated much higher by macroscopic research, and the thin sections confirm this.
The mineral content of the two rocks is also different. More feldspars were found in the yellow samples. Limestone grains are abundantly present in the cemented grey samples while the yellow rock does not show many. Lastly, the fossil content of the two samples differs. The grey cementated samples have many more remnants and the yellow rock does not show any.

5.2. Classification of samples

Macroscopic analysis already provided enough information to determine the nature of the sedimentary rock; a sandstone. However, both rocks are very different and can this can also lead to different names for the rocks. To determine the exact name of the rock, the Pettijohn classification is used. The figure used for classifying sandstone can be seen below in figure 5.2. Pettijohn classification uses four parameters: the percentages of quartz, feldspars, rock fragments and matrix. The percentage of matrix can be estimated using help figures which show percentages of minerals. The remaining three parameters should be found by using point counting. However, point counting was not done as this would be too time costly. Estimates of the amounts of quartz, feldspars and rock fragments were made. These percentages were plotted in a ternary diagram at the correct matrix percentage. The percentages for the samples are stated in table 5.1. The values for lithics were in some cases altered slightly to obtain a percentage of 100. This leads to the following classification for the samples:

Table 5.1: Percentages of Q,F,L and matrix, name and provenance.

Sample	% Quartz	% Feldspar	% Lithics	% Matrix	Name	Origin
L11	75	1	24	5	Sublithic Arenite	Recycled Orogen
L12	80	1	19	5	Sublithic Arenite	Recycled Orogen
S11	65	1	34	5	Lithic Arenite	Recycled Orogen
S12	60	2	38	5	Lithic Arenite	Recycled Orogen

5.3. Analyses of Diagenetic processes

The paragraphs above already mentioned some diagenetic processes which were visible in the sections. This paragraph will deal with the further description of the diagenetic changes of the samples. This will be done in general chronological order for compaction, dissolution and cementation. The order of diagenesis could not be seen by investigating the thin sections, but is based on literature (Nelson, 2013). Some diagenetic processes have only been discovered in one of the sample sets, whilst others are present in both sample sets.

5.3.1. Description of diagenetic processes

This paragraph will describe the diagenetic processes of compaction, dissolution and cementation. Evidence of these stages have been found in both sample sets.

The burial of the sediments will cause the first diagenetic process; compaction. The weight of overlying sediments will push the grains closer together. Once the pressure builds up, the grain contacts will experience higher pressures and this will lead to pressure solution. The quartz grains will dissolve partly into the pore fluids. When the pressure is increased even more, the contacts of the grains can slide into each other and sutured grains are created. Sutured contacts between two grains looks similar to a weld (B.1c)(Southard, 2007) and were found in both sample sets.

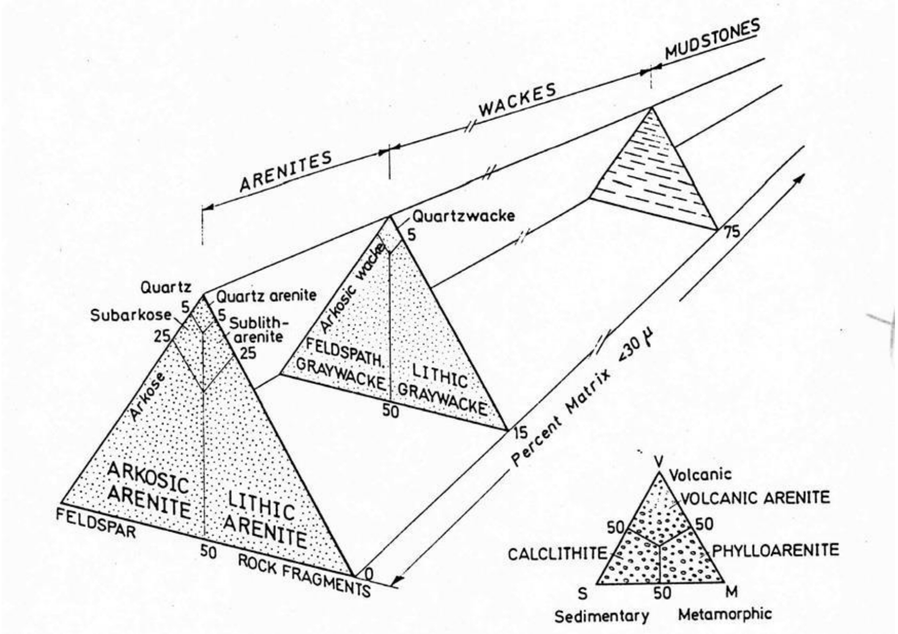


Figure 5.2: Pettijohn classification used to name the sandstones. From: Pettijohn *et al.*, 1987

Feldspars will dissolve and precipitate as clay minerals. No clay minerals are found however but literature states that Kaolinite is found in in similar outcrops in minor amounts and that it originated from feldspars (van den Brill and Swennen, 2008). It is assumed feldspars have been present in both sample sets and have dissolved.

After dissolution of feldspars and fossils the cementation phase probably started. Calcite cement is able to form when Ca^{2+} and $CO_3{}^{2-}$ ions are available. Ca^{2+} and $CO_3{}^{2-}$ ions are common in both marine and meteoric waters. They are formed from the chemical weathering of rocks and the dissolution of rocks or bicarbonates (Nelson, 2013). Cementation will start when the concentration of dissolved minerals in the pore fluids is too high. The pH of the waters is important for calcite cementation and quartz overgrowth as calcite will only precipitate when the pore fluids are alkaline, and vice versa for quartz cement. Jurassic sea waters are within the margin of pH so both quartz cement, and calcite cement can precipitate (Hönisch *et al.*, 2012). Meteoric water would be too acid for calcite to precipitate and it would dissolve instead. Quartz cement and calcite cement are present in both samples (figs. A.1a and A.1d). The L samples hold less calcite cement than the S samples. The reason for this will be put forward in chapter 6. The calcite cement in combination with the depositional history can be used to prove cementation took place close to the sea water and with marine water as pore fluids (van den Brill and Swennen, 2008).

Calcite cement will start to precipitate from a grain-pore boundary into the pore. Drusy cement will form on the grains and further into the pore, blocky cement will be formed (Donselaar, 2008). When enough water with sufficient ions passes through the sediments, the cementation will continue until the permeability is too low to allow further passing of fluids. Cement can also precipitate on a quartz grain, these corrosive calcite cements were clearly visible in the thin sections (figure A.1c).

5.3.2. Evidence of diagenesis in S Samples

In the well cemented grey rock, lots of limestone grains are found (A.1f). Very fine crystalline rounded calcite particles are found inside these grains. This leads to the conclusion these grains have a detrital source. To name the grains, the Dunham classification for carbonate sedimentary rocks was used and it turned out to be a mudstone (Dunham, 1962). Since the grains are detrital, this means they cannot be used to give more information about the depositional environment of the formation. The mudstone grains are more rounded than the quartz grains. Limestone grains are softer than quartz grains and this means they will weather more rapid. In other cases a more rounded grain indicates a longer transport, but no conclusion can be made for these samples.

Dissolved fossils (micritisation) were only found in the S samples figure (A.1b), but no clear explanation was found for this. The fossils were dissolved and calcite crystals precipitated. The dissolution of fossils will provide the pore fluid with extra carbonates as the fossils are made up of calcium carbonate. Echinoderms are known to have a magnesium calcite skeleton (Nichols, 2009). The fossils will partly dissolve, causing extra carbonates in the fluid. Occasionally the fossil completely dissolves, in the samples of this research this has not always been the case. Parts of the fossils can still be found (A.1b) and they are probably Echinoderms. This is a very large group of sea animals which have five radial symmetry (Morris, 2007). Echinoderms could live anywhere from the shore to the deep sea but the water needed to be salt enough as they cannot survive in waters with a low salt percentage (Nichols, 2009). This leads to a conclusion that the rocks have been deposited in a sea and not in the delta plain. The salt content close to the delta mouth will not be sufficient for the Echinoderms to survive.

5.3.3. Evidence of diagenesis in L Samples

Ferroan content was found throughout the samples and a few iron rich bands could be seen in the samples (B.1b). The high iron content in some parts of the sample could originate either from detrital minerals from the weathering products of the mountains, or it could be altered minerals which were present in the rock. The area of deposition was located in a tropic environment. This could have lead to the oxidation of iron minerals, which were then transported into the delta. If this is not the case, the iron could come from altered Pyrite, or the dissolution of minerals such as hornblende, biotite, olivine and others (van den Brill and Swennen, M.Aref, 2008, 2017). The iron would be oxidised by the oxygen inside the pore fluids.

5.4. Provenance of samples

The data from table 5.1 above can also be used to find the provenance of the sandstone.

The classification was first described by Dickinson in 1979. Dickinsons technique uses percentages of feldspar, quartz and lithics to find the provenance of a sandstone. To find the percentages of these, the same technique as described in paragraph 5.2 could be used. The Dickinson diagram as shown in figure 5.3 was used.

When the data from the samples are added in the diagram, the following provenances are found: all four samples are in the recycled orogeny section (figure 5.4). The differences between the data of the same samples is relatively small and these come from taking estimates. The grey samples contained more lithics than the yellow samples. The outcome of the provenance study fits the expectations. The history of the area described the orogeny which took place and the weathering products which are transported into the delta.

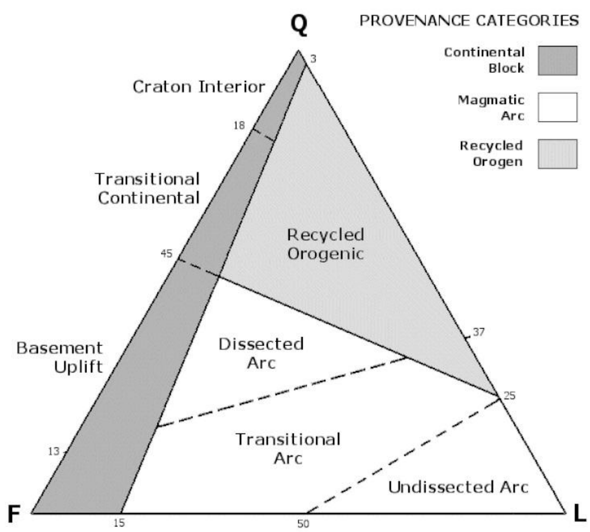


Figure 5.3: Dickinson classification for sandstones. From: Alden, 2013

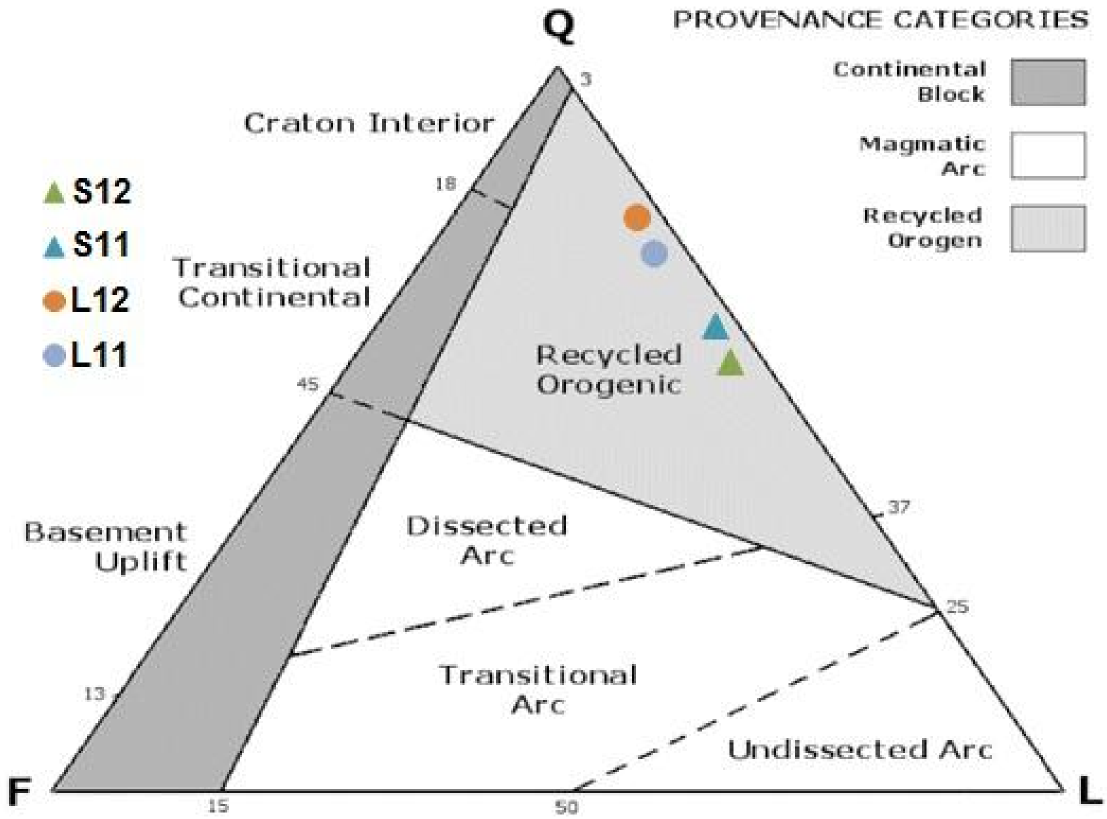


Figure 5.4: Dickinson Diagram with data points. Original from Alden, 2013.

6

Synthesis

The previous chapters described the geological setting, the outcrop and the microscopical features. Chapter 5 already looked into the diagenesis and the timeline of diagenesis. This chapter will deal with the complete diagenetic story and will put forward some options as to why the different weathering patterns are visible.

The Luxembourg Sandstone has been deposited in a tidal dominated delta. No evidence in the field could be found for the tidal delta, but multiple literature sources state this (van den Brill and Swennen, Mertens *et al.*, Berners, Molenaar, Guerin-Franiatte and Muller, 2008, 1983, 1983, 2009, 1986). However, enough evidence was found for a deltaic deposit. Firstly the sands grains. These are fine and angular which means they have been transported for a short period of time and are deposited in sand bars in the sea, relatively close to the coast. A deposition further inland would lead to larger grains and a deposition further away from the delta would lead to clays and higher limestone contents. The glauconite grains which are found were also very fine crystalline. Glauconite is formed in marine conditions (Nichols, Smith and Hiscott, 2009, 1984) which means these grains have either formed in the sediments which later formed the Luxembourg Sandstone, or the grain has formed before the formation of the Ardennes and has been transported from the mountains into the delta. Both possibilities confirm a deltaic deposition. The mudstone grains are detrital (see paragraph 5.3) and this means they have also been transported and deposited, not formed during deposition.
Secondly, the fossils which were found. Echinoderm can only survive in waters which are sufficiently salt which eliminates the possibility of alluvial deposits.
The transgressive regime of the sea strait can be proved by the marls and limestones deposited on top of the Luxembourg Sandstone (van den Brill and Swennen, 2008). The transgressive movement of the sea also ensured the formation would be submerged in marine waters until the late Jurassic (Maquil and Colbach, 2009).

The outcrop of the formation is characterised by horizontal beds of varying thicknesses and lenses. The horizontal beds do not show a rhythmical alternation between the two rock types. After having visited the outcrop, the reason for the different appearances and characteristics was found to be chemical weathering of calcite cement. The grey rocks were strongly cemented whilst the yellow rocks remained porous and had little cement. Microscopical research confirmed this.

The grey rocks hold lots of calcite cement and some quartz cement, while the yellow rock holds less cement. Calcite is weathered more easily than quartz (DiVenere, 2017), so the rocks which hold more calcite (the grey rocks) will be weathered more. These rocks have retracted into the outcrop as they have been dissolved by waters. Dissolution of calcite has already started before the uplift of the Pliocene with groundwater. After the uplift, weathering of the rock was probably sped up by wind, ice and water from rivers and rain.
The dissolution of calcite cement caused the formation to have the appearance it has today. The unusual distribution of that calcite cement throughout the formation has yet to be explained.
The following paragraphs will look deeper into the processes which affect the cement distribution. Three different variables affecting cementation will be put forward in this chapter as these could lead to the different cementation patterns. The final theory will be presented in the conclusion.

6.1. Variable 1: Permeability differences

As mentioned in chapter 5.3 in order for cementation to take place, carbonate ions are needed. The dissolved carbonate ions will need to precipitate from the pore fluids and nucleation sites will provide the possibility for this. Nucleation sites can be small limestone particles or fossils. Both the amount of nucleation sites and permeability are controlled by the fabric of the formation. The amount of carbonate which reaches the nucleation sites is dependant on the concentration of carbonates in the marine waters. Lets assume the carbonate content of the fluids are constant, then the amount of carbonate ions inside the sediment depends on the permeability of the sediment. If a sediment has a lower permeability, less water with carbonates will pass through the sediment and less cementation will take place (Molenaar, Marshall and Ashton, 2009, 1980).

One explanation for the difference in permeability could be clay content. A tidal dominated delta experiences tides and these cause the water to move in and out the delta. During high and low tide, slack water will occur. This calm water allows for clay to be deposited as only low energetic water allows clay to be deposited, while a more energetic flow of water holds the sediments in suspension (Nichols, 2009). Once the tides pick up, the flow of water will bring coarser material such as sands into the delta again and deposit them. The clay could cause the permeability reduction as it is very impermeable (Bjorlykke, 1982).

The above described phenomenon needs to be elaborated further. The cementation pattern of the outcrop of the formation is not regular at all and the morphology of a tidal dominated delta could explain this. Figure 3.5 shows one of these deltas and shows the sand bars. These sand bars are oriented parallel to the river and have irregular shapes. The above mentioned clay deposits could only be deposited in the subaqueous areas of the delta, which of course varies between high- and low tide. Some areas of the delta will not be submerged as often as others.
Once more sediments are deposited, the weight becomes larger and the sediments become buried. Some areas inside the sediment will contain more clay than others. Areas with low amounts of clay will create a path of permeability through the sediments.

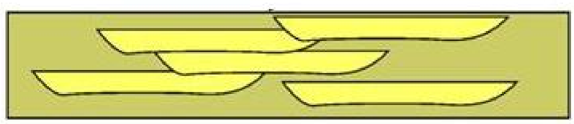


Figure 6.1: Fluvial deposits, channel fill. from :Nichols, 2009

Figure 6.1 shows a schematic image of alluvial channel fills but it can be used to illustrate the permeability changes mentioned above. The scale of the figure is several meters to dozen of meters for each channel fill. When several sand bars are deposited on top of each other and burial occurs, a similar cross section could be drawn. Now imagine that clay is also deposited somewhere next to these sand bars, then local permeability changes can occur. A path of permeable sands could arise, whilst the sand bars next to it, which could be as permeable, are not connected to permeable sands due to the clay. This feature could produce two identical sand bars with very different cementation patterns. Sands which were not connected to the well permeable sands will not receive the same amount of carbonate rich marine water and this will impede further cementation. The outcrop did not show these features exactly, however when looking at figure 4.5 a connection between lenses and beds can be found. This could mean that more connections between permeable sand bars are present.

No clay was found in the thin sections however but this does not exclude the permeability variable yet. Only four thin sections were used and it could be that no transition area with clay was looked into.

A second option regarding local permeability changes, concerns the distribution of grains. Tides play an important role in a delta. They are controlled by the moon and the sun and this is a cyclical occurrence. During spring tide, when earth, moon and sun are in line with each other, the tides will be highest. This creates a high energetic environment which facilitates the transport of coarser material further into the sea. A deposit which is made up of coarse material tends to be more permeable than finer deposits and if these coarser materials are deposited on top of finer grained sediments, it will create a transition (Bear, 1972). Another consequence of this is the sorting of the sediment as a more heterogeneous sediment sorting will cause lower permeability (Selley, 2000). However, the descriptions of the thin

sections do not show differences in sorting between the well cemented and the less cemented rocks, and this negative permeability consequence will not be taken into account.
During high energetic deposits, the coarse grained sands will allow more seawater to pass through and this will also influence the finer grained sands underneath. The sands below the coarse material could be cemented as well, whilst neighbouring sand deposits could be buried with finer material which are less permeable, causing less carbonate rich water to pass through and thus slow down the cementation process (Molenaar, Marshall and Ashton, 2009, 1980).

6.1.1. Residence time

The longer a sediment remains in contact with a carbonate rich fluid, the more calcite will precipitate and the more cemented it will become. This section will deal with the changes in residence time and how this could have affected the cementation of the sediments. The same scenario as in section 6.1 will be used and the effects of a higher permeability will be even larger. If a sediment gets buried very fast, it will not have much time in contact with the sea water. A sediment could get buried by a prograding channel, interrupting the direct contact with sea water, and thus impeding the cementation process (van den Brill and Swennen, 2008). The geomorphology of a delta changes rapidly and tidal channels are moved quickly. Once the sediment get buried, it will not stay in contact with carbonate rich marine waters and little cementation will take place. Coarser grained deposits as mentioned in paragraph 6.1 will have a smaller impact on the permeability than finer grained deposits.The above theory assumes fine grained sediments being deposited and thus impeding further cementation of the sediments. (Bear, 1972).

6.2. Variable 2: Carbonate content differences

Many mudstone grains were found in the grey rock samples, whilst none were found in the yellow rock. This could be an indication as to why the rocks show such different cementation patterns. As stated in paragraph 6.1, nucleation sites are necessary for cementation to take place. The mudstones are detrital which means their concentration in the depositions are dependant on the flow of the delta. Assuming constant permeability and fluid flow, if an area contained more mudstones, a stronger cementation pattern should occur, since more nucleation sites are present. The distribution of mudstone throughout the sediment could be influenced by the grain size. The coarser grains of mudstone could be deposited in the channels, an example could be a lag deposit. The finer materials are removed by the flow of water caused by the tides, whilst the coarser material remains in place. During storms or spring tide, more coarse grains will be deposited as well (Molenaar, 2009). These local coarser carbonate rich material concentrations would increase the amount of cement to form.

Fossils in the sediment are also related to this. As mentioned before, fossils consist of carbonate. The presence of a few echinoderms could create small scale lenses (10-30cm) which are also present in the outcrop of the Luxembourg Sandstone (figure 4.4) (van den Brill and Swennen, 2008).

6.3. Variable 3: Redistribution of carbonates

Variable 3 has been put forward in an article of van den Brill and Swennen (11) and considers the redistribution of carbonates. Carbonate grains are dissolved in water and precipitate in other areas (Eder, 1982). Fluids have dissolved carbonate from the uncemented rocks and transported them into cemented rocks, which caused more cement to form. This could be another answer as to why the yellow rock contained no fossils or mudstones as these have all been dissolved. This mechanism could not have occurred independent form the previous two options as it requires cemented and uncemented rocks. This option provides an answer for second generation cement forming. Second generation cementation has not been observed during the research and this variable is based on literature.

Another possibility is that all three variables have been acting on the sediment and the formation and they caused the cementation patterns. This would mean that a permeability difference, either caused by clay and/or coarse and fine material alterations, residence time differences and varying carbonate content have influenced the deposition of the formation. Later, the redistribution of carbonates might have played a role in further cementing the rock.

6.4. No geological explanation

The above three variables all assume that the sedimentological characteristics of the formation had an impact on the cementation. Another possibility is that cementation can not be linked to the geological history and that meteoric waters and weathering caused the outcrop to look like it does today.

7

Conclusions & recommendations

7.1. Conclusions

The Northern German Basin and the Paris Basin were connected by a sea strait which was located in present day Luxembourg. Weathered products from the Ardennes were transported and deposited in a tidal dominated delta during the Early Jurassic. These detrital products created the Luxembourg Sandstone which consists of fine, moderately sorted, angular quartz grains.

The outcrop of the Luxembourg Sandstone formation shows an odd weathering pattern. A hard grey sandstone is alternated by yellow porous sandstones either as horizontal beds or as smaller lenses. The formation's appearance is caused by the dissolution of calcite cement. The grey rocks are very well cemented whilst the yellow rocks do not hold much cement. Most of the cement is made up of calcite crystals but some small amounts of quartz cement is also present. Cementation of the sediments started soon after deposition in influence of marine waters. Carbonate rich pore fluids precipitated calcite crystals in the pores of the sediment. Some quartz has also been precipitated on quartz grains and this created syntaxial overgrowth. The cemented grey rocks shows some micritised fossils and opaque minerals. The less cemented yellow rock shows some Muscovite and Microcline crystals.

The exact reason some areas have been cemented, whilst other experienced less cementation is still unclear. It is probable the three variables, which have been put forward in chapter 6, have played a role in the diagenesis of the Luxembourg Sandstone. This means the sedimentological characteristics of the formation can be linked to the present day appearance of the outcrop. However, it is also possible that the geological history of the formation cannot be linked to the diagenetic changes, and that meteoric waters and weathering caused the formation to have the present day appearance.
This thesis favours the theory that the sedimentological history of the formation exerted an influence on the diagenesis.
Some areas have been cemented and others experienced less cementation and this is caused by changes in permeability, carbonate distribution and redistribution. Permeability alterations caused by deposition of clay and/or coarse material created more permeable paths through the sediments.
More permeable layers were provided with more carbonate rich fluids and these have subsequently been cemented more. This process took place in marine pore fluids. A permeability difference in combination with heterogeneous carbonate deposition caused the first cement generation to form. A combination of favourable fluid flow and an increase in nucleation sites caused the strong difference in cement precipitation to take place. A later carbonate redistribution from the less cemented rock into the cemented rock caused a second generation of cement to form. Echinoderms concentrations created smaller lenses.

The Luxembourg Sandstone was uplifted during the Pliocene and was now exposed to wind, rain and cold and this shaped the formation. Meteoric waters will have passed through the formation before the uplift. Groundwater can be present deep in the earth and these will have weathered the formation. Weathering from groundwater in and later meteoric waters have caused calcite crystals from the cemented layers to dissolve and create the formation which is now present. The less cemented rocks have not been weathered as much since quartz grains are better resistant to the slightly acid meteoric waters, this is why these rocks stand out in the outcrop.

7.2. Recommendations

The main issue with this research is the significance of the data. Even though multiple samples of different places at the outcrop were available, these all showed the same macroscopic features. A general distinction between the two rock types could be made but not more knowledge could be deduced from the samples. Only four thin sections were made from two rock samples and this greatly influenced the significance. It cannot be said whether the thin sections are a good reflection of the whole outcrop or that they show exceptional characteristics. As mentioned in chapter 6, a tidal dominated delta is not a constant depositional environment. The small amount of thin sections used does not represent the changing environment of a tidal delta. More thin sections are needed to prove that the description of the mineral composition of these samples is reliable for the rest of the outcrop.

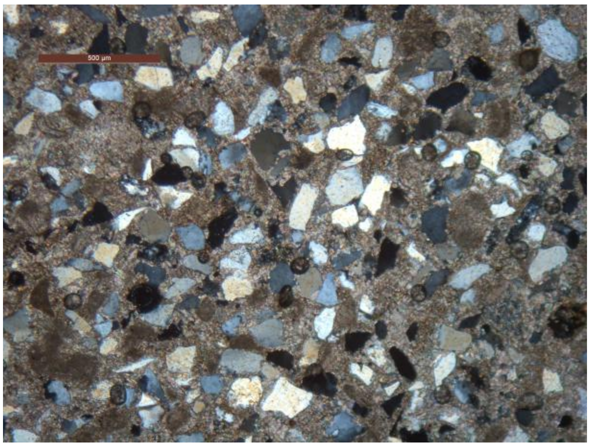
The uncertainty which arose when describing the sedimentological reason for the differences in rock could be removed by doing a more extensive fieldwork. The short fieldwork in this thesis did not provide the opportunity to look into the permeability or carbonate content differences described in the synthesis. If some of the described features are present at the outcrop then a stronger conclusion could be made. Since the permeability differences are an important parameter affecting the cementation, permeability measurements should be done. This data could be compared to other studies regarding the permeability dependence for cementation of sandstones. A better investigation using electron microscopy could provide more information about first or second generation cement.

The article of van den Brill and Swennen (11) proved to be very useful for this thesis. Their area of research was however far away from the outcrop near Echternach. A visit to this area could provide more answers and their description could be better compared to the findings in this thesis.

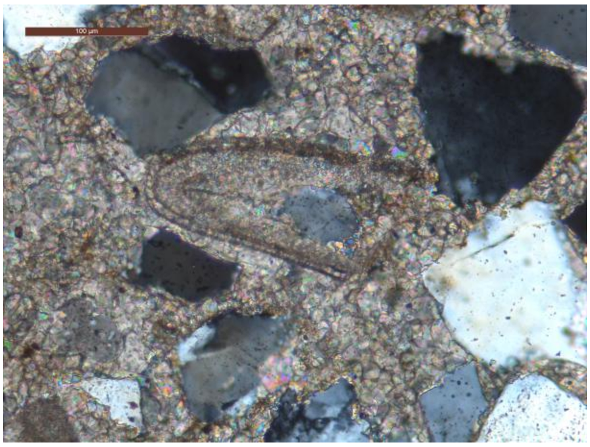
8
Acknowledegments

The author would like to thank his supervisor Drs. Maaike van Tooren for her assistance throughout the thesis. Maaike provided useful comments on draft chapters and helpful insights on the subject, even on her holidays. Ing. Wim Verwaal is thanked for his help. Jens Van den Berg for his patience and instructions about making thin sections and helping to produce them. Jaap Regelink for help in the laboratory and during microscopical research. Finally Dr. Joep Storms for a quick discussion about the sedimentological depositions of the Luxembourg Sandstone.

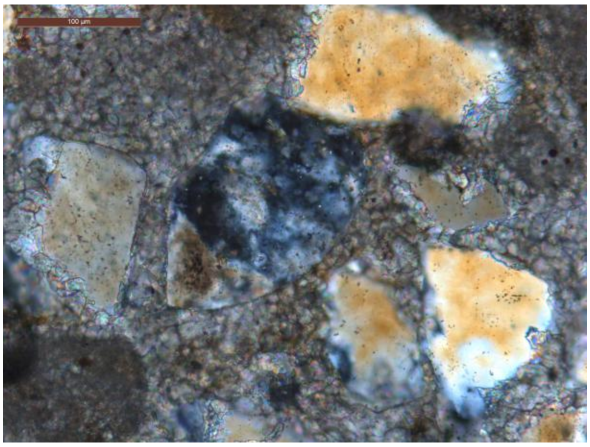
A. Plate 1



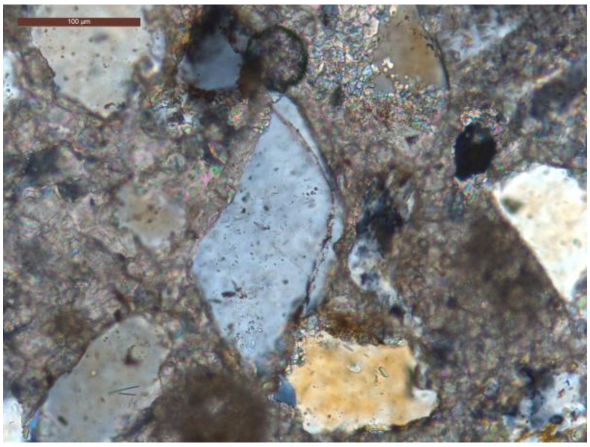
(a) S12.overview



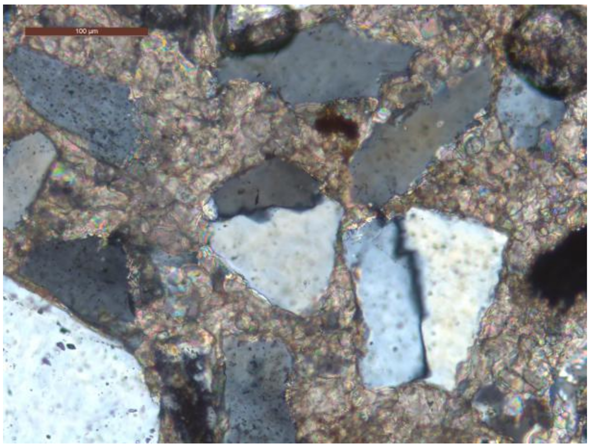
(b) S12. Micritised fossil filled up with cement and quartz grain.



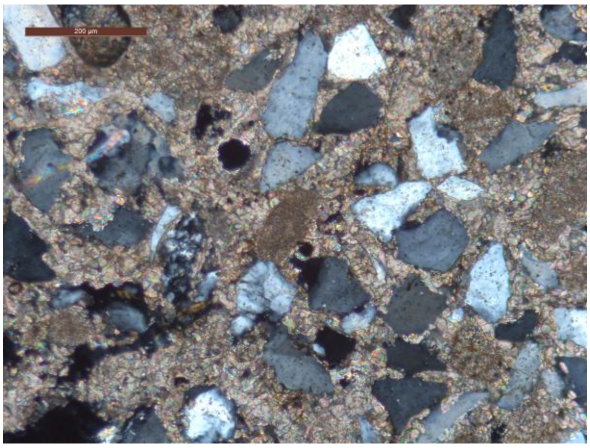
(c) S11. Corroded quartz grain with calcite crystals on the left. Polycrystalline quartz in the middle.



(d) S11. Syntaxial overgrowth on a monocrystalline quartz grain.



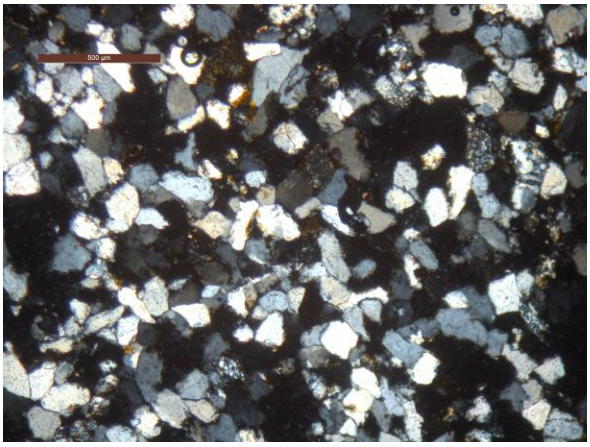
(e) S12. Sutured grains



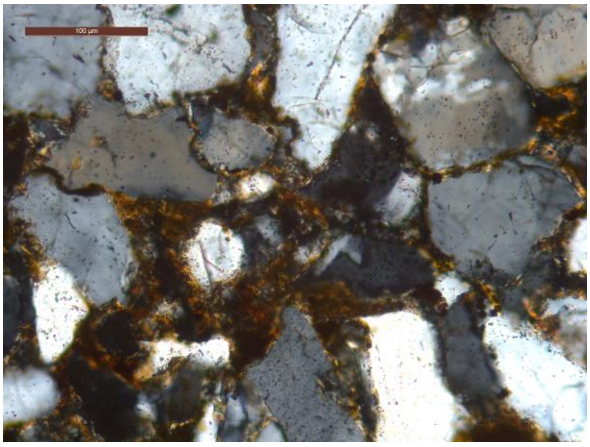
(f) S12. Limestone grain in the middle.

Figure A.1: Figures of thin sections S11 & S12.

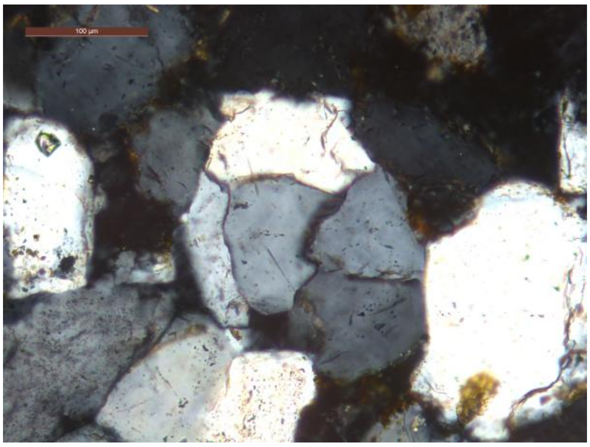
B. Plate 2



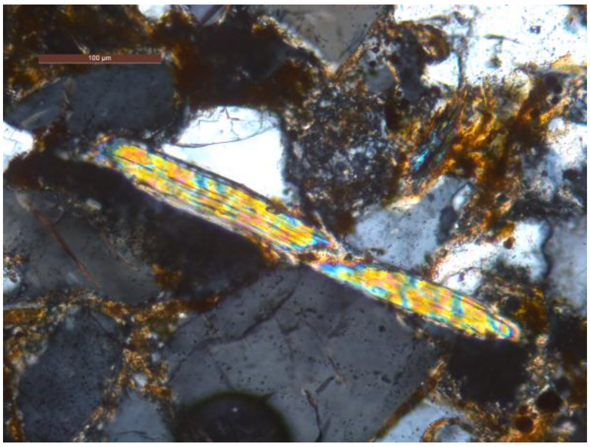
(a) L12. Overview



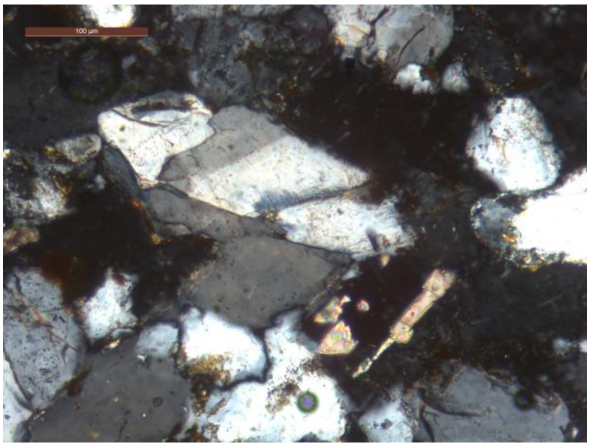
(b) L12. Quartz grains with ferroan cement in between.



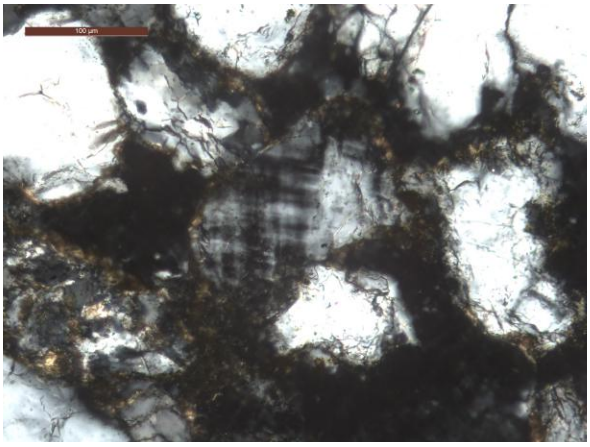
(c) L12. Sutured grains.



(d) L12. Muscovite Crystals.



(e) L11. Deformed Quartz



(f) L12. Microcline grain.

Figure B.1: Figures of thin sections L11 & L12.

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