



Universiteit Gent
Faculteit Wetenschappen
Vakgroep Geologie en Bodemkunde

Promotor: Prof. dr. Veerle Cnudde

Examencommissie: Prof. dr. Stephen Louwye
Prof. dr. Johan De Grave
Prof. dr. Luc Van Hoorebeke
Prof. dr. Veerle Cnudde
Dr. Ana Diaz
Dr. Timo Nijland.

Universiteit Gent
Faculteit Wetenschappen

Vakgroep Geologie en Bodemkunde
Krijgslaan 281, S8, B-9000 Gent, België

Tel.: +32-9-264.46.47

Fax.: +32-9-264.47.85



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Nederlandstalige samenvatting

In deze thesis wordt onderzoek gedaan naar methodes om de inwendige structuur van zandstenen en bij uitbreiding andere natuurstenen te analyseren. Aangezien natuursteen doorgaans bestaat uit elementen van heel verschillende grote-orde, is dit geen gemakkelijke opdracht. Zandstenen bestaan doorgaans uit korrels van enkele tientallen tot honderden micrometer in diameter, maar kunnen evengoed fijnkorrelige kleimineralen en microporiën met groottes rond de nanometer-schaal bevatten. Door deze typische multi-schaal eigenschappen van natuursteen, zijn verschillende technieken nodig om de eigenschappen van gesteentes helemaal te doorgronden. De poriëngrootteverdeling van natuursteen heeft een grote invloed op de manier waarop vloeistoffen door deze gesteentes bewegen, en dus hoe natuursteen gebruikt in gebouwen zal interageren met zijn omgeving en zal verweren of verouderen. Daarnaast bepalen de eigenschappen van een gesteentes poriesysteem de mogelijkheid tot het winnen van olie en gas of water uit natuursteenlagen en hoe snel of traag vervuilende stoffen zich doorheen het materiaal kunnen verspreiden.

Dit werk begint met een uitgebreide introductie over de eigenschappen van natuursteen en het belang van de karakterisatie ervan. Daarmee samen worden de belangrijkste onderzoeksvragen van dit doctoraat en van dit onderzoeksgebied algemeen aangehaald. In het vervolg van het inleidend hoofdstuk wordt dan kort uitgelegd hoe deze karakterisatie zal worden aangepakt. In dit werk wordt vooral gebruik gemaakt van methodes die een materiaal analyseren op basis van driedimensionale beelden. Tot deze methodes behoren zowel klassieke microscopie-methodes, die al tientallen jaren gebruikt worden door geologen, als hoogtechnologische en vernieuwende methodes zoals X-stralen tomografie en ptychografische tomografie. De introductie gaat verder met het uiteenzetten van de aanpak die doorheen deze thesis zal gehanteerd worden.

In hoofdstuk 1 worden de voornaamste klassieke microscopiemethodes

uitegelegd. Deze methodes zijn petrografische analyse met behulp van optische microscopie en scanning electronen microscopie, en worden al vele tientallen jaren gebruikt door geologen. Beide methodes worden gebruikt voor tweedimensionale beeldvorming van gesteentes en sedimenten, en hierover is over de jaren enorm veel kennis en expertise vergaard. Toch wordt ook met betrekking tot deze microscopische technieken nog steeds vooruitgang geboekt, en worden deze methodes nog steeds betrokken in vernieuwend en uitdagend onderzoek. Daarna worden in hoofdstuk 2 de belangrijkste materialen waarop onderzoek gedaan werd in deze thesis geïntroduceerd. Voor dit onderzoek werden drie verschillende zandstenen gekozen: de Duitse Bentheimer zandsteen, de Franse Vogezenzandsteen en de Indische Kandla Grey zandsteen. De Bentheimer zandsteen werd gekozen om zijn simpele structuur die typisch bestaat uit een stapeling van kwartskorrels met een weinig cement tussen deze korrels. Daarnaast kan een kleine hoeveelheid kleimineralen aanwezig zijn in het gesteente. Bentheimer zandsteen wordt mede door deze eenvoudige structuur zeer vaak gebruikt als analoog voor een reservoirgesteente, zowel als basis voor vloeistoftransport simulaties als echte experimenten in het labo. De Vogezenzandsteen of Meule zandsteen is afkomstig uit de Vogezen in Frankrijk, en is zowel qua samenstelling als structuur ingewikkelder dan de Bentheimer zandsteen. Naast kwarts bestaat de Meule zandsteen voor een groot deel uit veldspaat en kleimineralen die ervoor zorgen dat het porienetwerk van de Meule zandsteen bestaat uit zowel grote als kleine poriën. Hierdoor is het een pak moeilijker om de volledige structuur van het gesteente in beeld te brengen. Daarnaast ligt de uitdaging bij de Meule zandsteen ook in het vatten van de mineralogische variatie in het gesteente, aangezien de veldspaat, kleimineralen en ijzeroxides onregelmatig verdeeld zijn in het gesteente. Kandla Grey tenslotte is een gesteente dat de laatste decennia op enorme schaal werd geïmporteerd in West-Europa, en daardoor een belangrijke rol vervult als bouwsteen in deze regio. Het gesteente bestaat voor het grootste deel uit kwarts, maar ook voor ongeveer 15 procent uit veldspaat en een kleine hoeveelheid kleimineralen. Het zijn deze kleimineralen die voor preferentiële paden voor wateropname zorgen en aldus zwakke zones in het gesteente vormen.

Hoofdstuk 2 is volledig gewijd aan de principes en applicaties van X-stralen tomografie, de belangrijkste techniek in dit onderzoek. Dit hoofdstuk bespreekt na een algemene introductie van de methode ook de recente ontwikkelingen en systemen die beschikbaar zijn op het centrum

voor X-stralen tomografie van de Universiteit Gent, het UGCT. X-stralen tomografie, kortweg CT (*Eng: Computed Tomography*), wordt gebruikt voor het creëren van driedimensionale volumes waarmee de interne structuur van een gesteente kan bekeken worden. In het bijzonder wordt in deze thesis gebruikt gemaakt van micro-CT, dus CT met een resolutie van 1 tot enkele micrometer. Gedurende de laatste jaren is dit een standaardmethode geworden binnen vele takken van het geologisch onderzoek, zoals hydrogeologie, petroleumgeologie, paleontologie en sedimentologie. De sterkte van de methode ligt in het analyseren van de structuur van gesteentes, wat kan op verschillende monstergroottes, gaande van 1 millimeter tot enkele centimeters. Helaas kan de hoogste mogelijke resolutie niet meer gehaald worden op deze grotere proefstukken, en heeft de methode belangrijke beperkingen voor het analyseren van de mineralogische samenstelling van gesteentes. Naast CT op zich wordt in dit hoofdstuk ook aandacht geschonken aan driedimensionale beeldanalyse en beeldverwerking, twee enorm belangrijke stappen als men kwantitatieve resultaten uit CT gegevens wil halen.

In hoofdstuk 3 worden vervolgens enkele andere driedimensionale analysemethodes besproken, en dit keer gaat het om hoogtechnologische methodes die gebruikt worden om 3D beelden met heel hoge resolutie in de orde van enkele tot enkele tientallen nanometer te produceren. In het bijzonder gaat het om SEM gecombineerd met een gefocuseerde ionenstraal en ptychografische tomografie. Deze methodes zijn meestal vrij duur en weinig beschikbaar, en kunnen slechts gebruikt worden voor het bestuderen van kleine volumes, meestal minder dan ongeveer 100 micrometer in diameter. Daardoor kunnen deze methodes zelden als op zichzelf staande methode gebruikt worden om een heterogeen materiaal als natuursteen te bestuderen, en moeten ze gezien worden als een complementaire techniek naast meer klassieke onderzoeksmethodes.

In hoofdstuk 4 volgt een uiteenzetting van een mogelijke werkwijze voor het combineren van verschillende methodes om tot een totaal overzicht van zowel de structuur als samenstelling van een zandsteen te komen. Concreet werd CT op verschillende resoluties in dit hoofdstuk gecombineerd met SEM en elementanalyse met behulp van energie-dispersieve spectroscopie (EDS), op een kubusvormig stuk Meule zandsteen van ongeveer 15 mm groot. Door middel van beeldregistratie werden 2D beelden onderling met elkaar gelinkt en werden deze 2D

beelden vervolgens aan een 3D CT volume gekoppeld, waardoor korrel per korrel de samenstelling van het CT oppervlak kon worden bekeken. Deze koppeling geeft een pseudo-driedimensionale weergave van deze samenstelling, waardoor de ruimtelijke oriëntatie van bijvoorbeeld ijzerrijke laagjes kan worden weergegeven. Daarnaast werd ook 3D-naar-3D beeldregistratie toegepast, om het kleine kerntje dat uit het grotere basisstaal werd genomen te oriënteren in dit grotere staal. Aangezien de Vogezandsteen zowel qua structuur als samenstelling heterogeen is, is het belangrijk om te weten van welke zone de eigenschappen in verband met porositeit en samenstelling op hoge resolutie werden bestudeerd.

Hoofdstuk 5 focust op hoge-resolutie beeldvorming van de kleimineralen die in Vogezandsteen en Kandla Grey aanwezig zijn met behulp van ptychografische tomografie. Deze experimenten werden uitgevoerd op het Paul Scherrer Instituut in Zwitserland, aan de cSAXS stralingslijn. Met deze methode werden zeer kleine monsters (25 - 50 μm) geanalyseerd, met resoluties tot 45 nm. Met behulp van de methode werd zowel de microstructuur van kleimineralen op unieke resoluties gevisualiseerd als onderzocht uit welke mineralen de monsters precies bestonden. Daarnaast kon doordat de methode niet-destructief werkt gekeken worden wat het effect van een veranderende relatieve vochtigheid was op de structuur van de monsters. Meer bepaald kon gekeken worden naar de uitzetting van deze kleimineralen bij hogere relatieve vochtigheid. Ptychografische tomografie bewijst zich in dit hoofdstuk als een zeer veelbelovende methode voor het onderzoek naar de kleinste partikels in geologische materialen.

Terwijl de vorige hoofdstukken allemaal focusten op methodes om de porie-eigenschappen van natuursteen nauwkeurig te bepalen, wordt in hoofdstuk 6 gekeken naar de mogelijke toepassingen voor deze resultaten. In dit hoofdstuk wordt onderzoek gedaan naar de correlatie tussen experimenteel bepaalde eigenschappen van natuursteen, de bepaalde porie-netwerk eigenschappen en gesimuleerde en gemeten waarden voor permeabiliteit. Uit dit hoofdstuk blijkt dat er een zeer goede correlatie bestaat tussen capillariteit en permeabiliteit, en dat het ter plaatse meten van de permeabiliteit op gebouwen een goed alternatief kan zijn voor het nemen van stalen om de capillaire opnamesnelheid te bepalen.

Tenslotte illustreert hoofdstuk 7 de eerste resultaten behaald met het nieuwe systeem van UGCT en XMI: Herakles. Herakles is nog steeds in

de ontwikkelingsfase en combineert een μ CT scanner met een X-stralen fluorescentie (XRF) systeem. Met XRF kan de chemische samenstelling van een staal bepaald worden, en door de combinatie met CT kan structurele informatie direct gelinkt worden met de samenstelling op een bepaald punt. De resultaten in hoofdstuk 7 zijn nog steeds zeer voorlopig en tonen enkel een kort bewijs van het concept van de methode die kan gehanteerd worden met Herakles. Desalniettemin zijn deze resultaten veelbelovend en tonen ze de enorme mogelijkheden van het systeem, eens het volledig operationeel zal zijn.

Dit werk toont dat μ CT een heel belangrijke methode is voor multi-schaal analyse van geologische materialen, met talloze toepassingen in alle geologische subdisciplines. μ CT heeft echter ook enkele belangrijke limitaties, zoals het gebrek aan chemische informatie die kan bekomen worden en het feit dat er geen ultra-hoge resoluties kunnen bereikt worden. Daarom wordt aangetoond dat de combinatie van μ CT met traditionele microscopiemethodes en vernieuwende, hoge-resolutie 3D beeldvormingsmethodes een totaalbeeld van de structuur en samenstelling van gesteentes kan produceren, van de nanometer- tot de centimeterschaal. In de toekomst zal de verdere ontwikkeling van het Herakles systeem een directere link tussen zowel samenstelling als structuur met zich mee brengen. Helaas zal dit nog altijd slechts mogelijk zijn op zeer kleine proefstukken, en zal een gecombineerde aanpak met complementaire methodes zoals SEM/EDS noodzakelijk blijven. Verder onderzoek zal dan ook inzetten op de verdere automatisering en stroomlijning van het data-fusie proces tussen μ CT en microscopie. Daarnaast moet ook proefstukvoorbereiding van zeer kleine proefstukken van enkele tientallen tot honderden micrometers beter worden, zodat deze kunnen worden gebruikt voor ptychografische tomografie of ultra-hoge resolutie X-stralen tomografie.

English summary

In this thesis, research is performed on methods to analyse the internal structure of sandstones and other natural stones. Since natural stone contain elements of very different sizes, this is by no means an easy task. Sandstones generally consist of grains several tens to hundreds of μm in size, but can just as well contain fine-grained clays and micropores of nanometre-size. This typical multi-scale characteristics create the need for multiple methods to fully comprehend the properties of natural stone. The pore size distribution of natural stone has a great influence on the fluid transport inside these stones, and therefore on the way building stones will interact with the environment and how they will weather and age. Furthermore, pore network properties control the possibilities for the extraction of oil, gas or water from reservoirs and aquifers and the rate of pollutant spread through the ground.

This work starts with an elaborate introduction on natural stone properties and the importance of their structural and chemical characterisation. Further, the most important research question of this thesis and the research field in general are formulated. The introduction continues with an explanation of the approach that will be used for this characterisation. In this case, three-dimensional image-based analysis methods are used. Not only classical microscopy methods that have been used for many decades are used in this work, but also high-end innovative methods such as X-ray tomography and ptychographic tomography.

In chapter 1, the most important classical microscopy methods are explained: petrographical analysis by means of optical microscopy and scanning electron microscopy (SEM). Both methods are used for two-dimensional imaging and are very mature methods in geology. Nevertheless, these methods are still used in ground-breaking research and technological and methodological progress is made even today. Consecutively, chapter 1 discusses the most important materials used in

this thesis. Three different sandstones are used: the German Bentheim sandstone, the French Vosges sandstone and the Indian Kandla Grey sandstone. Bentheim sandstone is the most simple sandstone of the three, and consists mainly of quartz grains, with a low amount of cement and clay minerals between the grains. Due to this simple structure it is often used as an analog for reservoir rock, both in simulations as real-life experiments. The Vosges sandstone, a pink sandstone from the French Vosges mountains, is both in terms of structure and composition more complicated than Bentheim. Besides quartz, a large amount of feldspars and clay minerals are present, causing a pore structure with large and small pores. The Indian Kandla Grey sandstone finally, consists mostly of quartz and feldspars, and has a very low amount of clay minerals in its structure. It are these clay minerals that cause preferential paths for fluid absorption and therefore cause weak areas in the stone.

Chapter 2 is completely devoted to X-ray tomography, the most important method in this thesis. This chapter discusses, after a general introduction of the method, also the recent developments and systems that are available at the Centre for X-ray Tomography at Ghent University (UGCT). X-ray tomography (CT) is used to create 3D volumes that allow analysis of the internal structure of a rock. In this thesis, micro-CT (μ CT) is used, this is CT with a resolution of 1 to several micrometre. During the last years μ CT has become a standard method in many fields of geological research, such as hydrogeology, petroleum geology, paleontology and sedimentology. The strength of the method lies in the analysis of rock structure, which can be done on samples from 1 millimetre to several centimetre. Sadly, the highest resolution cannot be reached at these larger samples and the method has important limitations in terms of analysis of the composition of stones. Apart from CT, this chapter also introduces 3D image analysis and processing, two steps that are of paramount importance to produce quantitative results from μ CT data.

Chapter 3 discusses a number of different 3D imaging methods, which are high-end methods that produce 3D images with very high resolutions, in the order of a couple of tens of nanometre. These methods are focused ion beam combined with SEM (FIB-nt) and ptychographic tomography. These methods are generally quite expensive and have low availability. Furthermore, they can only be used for the analysis of very small volumes, generally less than 100 μ m in diameter. Therefore, these methods can rarely be used as the single method to study a heterogeneous material such

as natural rocks, and they have to be seen as complementary technique besides more classical methods.

In chapter 4, a possible workflow for the combination of different methods to study structure and composition of stones at multiple scales is explained. In practice, μ CT at different resolutions was combined with SEM and chemical analysis using energy-dispersive spectroscopy (EDS) on a cuboid Vosges sandstone sample with a size of about 15 mm. Using image registration, 2D images were linked to each other and after that, these 3D images were linked to a 3D CT volume. This way, grain to grain mineralogy could be determined and a pseudo-3D look into the distribution of different mineral phases could be provided. From the 15 mm cuboid sample, a 1 mm microplug was extracted for high-resolution μ CT. Using 3D-to-3D image registration, this small microplug could be located in its bigger source sample, which is important since the Vosges sandstone is heterogeneous in structure and composition. By performing this step, it is possible to address the parameters that are obtained from high-resolution CT to the correct region in the main sample.

Chapter 5 focusses on high-resolution imaging of the clay minerals inside the Vosges sandstone and Kandla Grey, by means of ptychographic tomography. These experiments were performed at the cSAXS beam line of the Paul Scherrer Institute in Switzerland. Using this method, very small samples (25 - 50 μ m) were analysed, at resolutions down to 45 nm. Not only the microstructure of the samples could be visualised, but the minerals that were present in these samples could also be identified. Since this method is non-destructive, the effect of a changing relative humidity on the clay mineral samples was evaluated, and the swelling of these clays at high relative humidity was shown. Ptychographic tomography proves itself in this chapter as a very promising method for the research on the smallest particles in geological materials.

While the previous chapters were focused on methods to accurately determine pore network properties, chapter 6 shows a possible application of these results. In this chapter, we studied the correlation between experimentally determined natural stone characteristics, pore network properties and simulated and measured permeability values. This chapter shows a very good correlation between the capillary absorption coefficient of stones and their permeability, which was explained by the imaged pore network properties. Therefore, in situ measurements of permeability on buildings might prove a valid alternative for capillary absorption

determination. Unlike the latter method, measuring permeability does not require destructive sampling of buildings and monuments, and additionally, this method can be performed very fast with straight-forward result interpretation.

A final chapter shows the first results of UGCT's and XMI's latest system: Herakles. Herakles is still under development and combines a nano-focus μ CT scanner with a confocal X-ray fluorescence (XRF) system. Using XRF, the chemical composition of a sample can be determined, and by combining this with a μ CT system, structural information can directly be linked to the chemistry at a certain point. The results in chapter 7 are still very preliminary and only show a brief proof of principle of the XRF / μ CT combination that Herakles provides. However, these results are very promising and show the great possibilities of the system, once it will be fully operational.

This work shows that μ CT is a very important tool for the multi-scale analysis of geological materials, with countless applications in all geological fields. However, μ CT has important shortcomings such as the lack of chemical information and the inability of imaging at extreme high resolutions. Therefore, we show that a combination of μ CT with other traditional microscopy methods and high-end, high-resolution 3D analysis methods can create a total overview of both the structure and composition of rocks, from nanometre to centimetre-scale. In the future, the further development of Herakles will provide a more direct link between microstructure and chemical composition, however, this will only be possible on small, millimetre-sized samples, so the need for other complementary methods such as SEM/EDS will still remain. Therefore there will be a need for additional research in the automatisisation or streamlining of data-fusion between μ CT and microscopy methods. Future efforts should be done in sample preparation of very small samples in the micrometre-range, that can serve as samples for ptychographic tomography or ultra-high resolution X-ray tomography.

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Introduction

0.1 The multi-scale nature of natural stones

Natural stones or rocks can be defined as a solid substance that occurs naturally because of the effects of three basic geological processes: magma solidification, sedimentation of particles, and metamorphism (a process that changes the original stone due to temperature and pressure changes). As a result of these processes, three main types of rock occur: igneous rocks, sedimentary rocks and metamorphic rocks.

Sedimentary rocks can be roughly divided into four principal groups (table 1, Tucker (1981)) : *siliciclastic or detrital rocks*, are rocks that consist of fragments, grains or clasts of preexisting rocks that have been transported and redeposited after the weathering of the host rock. *Biogenic or biochemical sediments* are mainly limestones, created by biological activity, but also phosphate deposits or coal deposits belong to this group. *Chemical sediments* such as evaporites are created by chemical processes and *volcaniclastic sediments* such as tuffs are formed during volcanic eruptions.

Siliclastic	Biogenic / Biochemical	Chemical	Volcaniclastic
conglomerates	limestones	evaporites	e.g. tuffs
breccias	dolomites	ironstones	
<i>sandstones</i>	cherts, phosphates		
mudrocks	coal, oil shale		

Table 1: The four main groups of sedimentary rocks: Siliciclastic, biogenic, chemical and volcaniclastic. Sandstones belong to the siliciclastic group. From (Tucker, 1981).

Siliciclastic rocks can be further divided according to their grain size.

Claystones have a grain size lower than 4 μm and siltstones have grain sizes between 4 and 62.5 μm . Both rock types can be attributed to the mudrock category. Rocks with grain sizes over 2 mm are called conglomerates or breccias (Tucker, 1981). In this work, emphasis is put on *sandstones*, which are rocks that have a dominant grain size between 2 mm and 62.5 μm (figure 1) according to their definition and were often deposited in shallow marine environments, rivers or lakes (Pettijohn et al., 1973). The composition of a sandstone's grains can be any clastic material (e.g. quartz, organic materials, volcanic debris, rock fragments, etc.). According to the origin and composition of these grains, sandstones can be classified into different groups according to the Pettijohn classification (figure 2): *quartz arenites* contain over 90 % quartz, *arkoses* contain more than 25 % feldspars and *litharenites* contain more than 25 % of rock fragments. *Wackes* are sandstones which are poorly sorted, with more than 10 % of grains smaller than 30 μm (Dott, 1964).

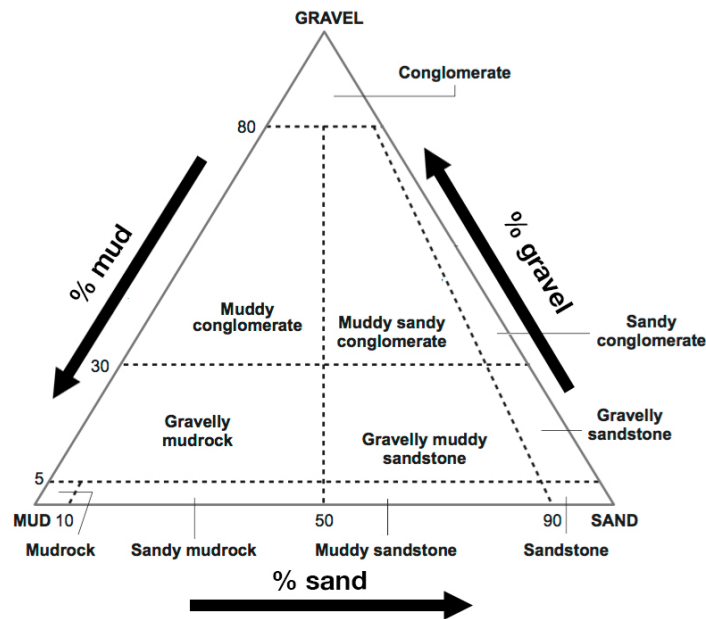


Figure 1: A: division of siliciclastic rocks into different groups according to their grain size. Adapted from (Nichols, 2009).

Rocks are important in many aspects of science: they are the host of our oil and gas reserves, serve as building stones for our monuments and are

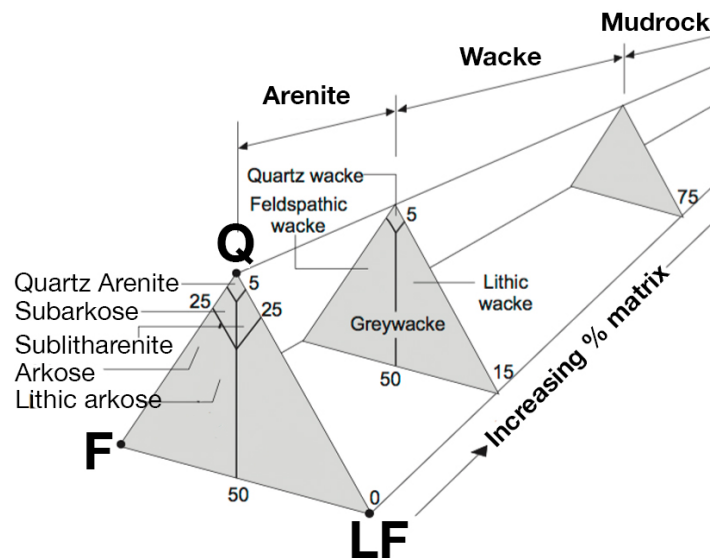


Figure 2: Pettijohn classification of sandstones according to main components. Q = quartz, F = feldspars, L = lithic fragments. Adapted from (Nichols, 2009).

the host material for (precious) metals and gems. Furthermore diagenesis processes can preserve traces of the history of the earth and everything living on it. All rocks are composed of minerals and empty spaces, which are pores or fissures or cracks. The pore geometry, size, specific surface area, grade of connection and their geometrical distribution strongly affects many different aspects of the behaviour of stone over time. An important difference between stones and rocks can be made here. Although both words have similar meanings, *rock* is generally used for the unaltered geological material, while the word *stone* implies human interaction or use with this material has been performed.

Characterising the structure of rocks is of key importance to understand their behaviour, and therefore it is crucial to know that all rocks, and sedimentary rocks in particular, are typically 'multi-scale' objects or entities. Inside rocks, there are features that are as small as a few nanometres, e.g. fine layers of clay minerals or the pores between them. On the other side of the scale, there are large fractures or formations, that can govern the flow properties inside oil or water reservoirs. Between these two extremes, there are features at every length scale: individual

grains that can be from a few hundreds of nanometres to a millimetre in diameter; small nanopores can form the connection between large, so called vuggy porosity; stones can be used as building blocks of a few decimetres that are combined into a building of 50 metres; and these stones itself are excavated in quarries that can be hundreds of metres in size. A rough boundary can be set between the *pore scale* and the *field scale*, where everything below a few millimetres can be considered as pore scale (figure 3). At the transition between pore and field scale, we would like to add a *core scale* or *lab scale*, which corresponds to the size of most samples that are used to study both the pore scale and the field scale, being around 5 to 100 mm.

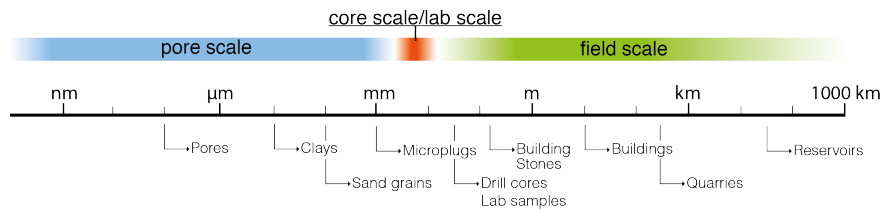


Figure 3: Schematic representation of the pore and field scale in geomaterials research, with different types of features at different scales.

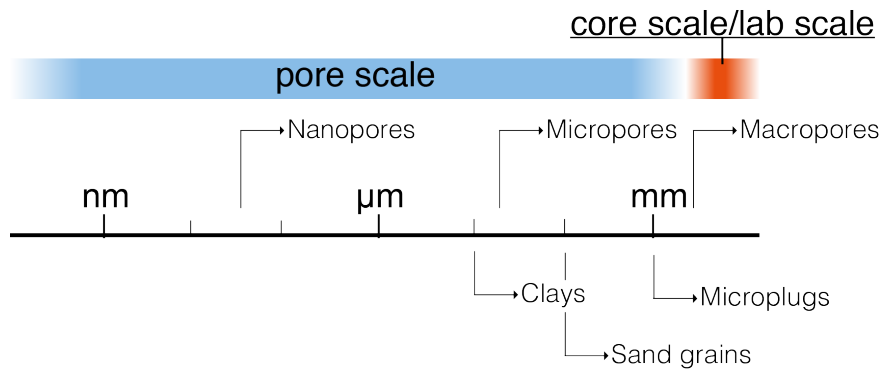


Figure 4: Detail of figure 3 showing the pore scale, which spans about 8 orders of magnitude.

The main focus of this thesis lies in the characterisation of the pore space of rocks. The reason to do so is that processes happening inside this pore space direct the behaviour of rocks on a larger scale. Although focusing only on the pore scale might seem a large simplification, figure 4 shows that this pore scale spans 8 orders of magnitude by itself. In sandstones,

the largest pores are defined by the shape and size of the quartz grains, while most of the smallest pores are voids between authigenic, pore-filling clay minerals such as kaolinite, smectite and illite (Jamtveit, 1997). Each of these clay minerals has its own characteristic shape, size and influence on fluid flow. In general, there is a crucial interrelation between the internal microstructure of the minerals/pores and its chemical composition, therefore, one is obliged to examine not only the microstructure but also the chemical components of the stone, if one wants to understand and model the macroscopic features of the material.

0.2 Scientific background

The ultimate goal of this thesis is the structural and compositional 3D characterisation of minerals and pore-structures at a pore-scale level, over the entire size range of this pore scale. As no method exists that is capable of high-resolution imaging on samples that are large enough to be representative for an entire stone, one method could be to couple information from for example μ CT with data acquired by other 2D and 3D imaging techniques.

A full 3D characterisation of a stone's structure and composition is important for many reasons, and to date the internal dynamic processes occurring at a pore scale level inside natural stones are in general still poorly understood. In the research field concerning natural stones used as building materials, we are currently not able to predict how a stone will behave under well-defined climatic conditions in time and space. Studying the structure of the pore space from a nanometre to centimetre scale will provide valuable information on this behaviour. The main challenges in this characterisation process lie at the low end of the size scale (figure 4), i.e. in the observation and analysis of microporosity and fine-grained micas and clay minerals. It has been known for a long time that the behaviour of the clay mineral fraction inside sandstones has a great effect on the durability and water management properties of natural building stones (Cnudde et al., 2013; Winkler, 1968). Clay minerals inside natural stones are responsible for filling of pores, creating very narrow pores, and enabling preferential flow paths for uptake of water. Therefore, they have a great influence on permeability and strength of natural stone, thus on the durability of buildings and monuments. Clay minerals can have unique

swelling behaviour, responsible for stresses inside building stones, eventually leading to aesthetical or even structural damage (Wangler et al., 2011; Gutiérrez et al., 2012) in the form of scaling, crack formation and preferential erosion of certain surfaces (Ruedrich et al., 2011). Even when the present clay fraction does not consist of swelling clays, they can act as preferential paths for capillary water absorption, making the entire stone more susceptible for frost weathering (Cnudde et al., 2013; Winkler, 1968). As the morphology of clays and other phyllosilicates changes due to changing humidity, we would like to characterise the physical changes inside a pore network induced by fluid migration. Furthermore, the effect of the morphology and changes in this morphology of the pore network to the rate of fluid absorption, drying and permeability of sandstones needs to be assessed. In order to be able to study or model the contribution of these fine-grained minerals to the overall properties of the stone, not only the morphology of the individual clay mineral clusters needs to be determined, but also their distribution and place in the larger context of the stone.

Up until now, the water uptake and swelling behaviour of clay minerals and other fine-grained phases in building stones has been studied on a macroscopical scale. Expansion or damage due to these minerals was observed and monitored on laboratory-scale samples (Weiss et al., 2004), and the minerals responsible for these effects were identified using analytical techniques like X-ray diffraction (Sebastián et al., 2008) on a bulk sample of the stone. In order to fully understand these processes, there is a need for in-situ observation of clay mineral's behaviour and distribution, coupled with direct identification of these minerals. This requires imaging at very high resolutions of both the structure and chemical composition of these minerals. Furthermore, dynamic imaging of the expansion or shrinking of individual grains under different external conditions would help to understand the macro-scale processes inside natural building stones.

Besides the research field of natural building stones, we are also interested in how the narrowest pores influence fluid flow in natural stones in general, e.g. for hydrocarbon transport modelling, predicting the effects of water reclamation and studying the evolution of ground water pollution around dump sites or NAPL leaks. Pore scale modelling of fluid flow in geological materials has become an important part of geoscientific research (Blunt et al., 2002). By modelling transport and distribution of fluids in the pore space of a material, problems at larger scales can be

better understood and solutions can be found. While petroleum geology is the first field that comes into mind when thinking about the transport properties of rocks, this is equally important for water reclamation and remediation in aquifers or the use of natural clay barriers in waste disposal areas. While this modelling can be done directly on the images of a stone's microstructure, it is possible to process these images and extract a geometric model of the pore space, or pore network model (PNM) (Köhne et al., 2011; Bultreys et al., 2015). The main reason for doing so is the large reduction in computational demands when calculating properties on a PNM. Since heterogeneous materials like rocks often require a volume that is representative (the representative elementary volume or REV), to allow for correct calculations, PNMs are often a necessity. In these PNMs, pores and connections between them are represented with balls and sticks and these representations are used for the modelling of the stone's transport properties.

Both in direct modelling and modelling on PNMs, a correct and adequate description of the pore space is needed. The quality of the results is directly linked to the quality of the images that were used to decide which parts of a material are considered as voids and which as solid. In certain materials, e.g. tight sandstones, computed tomography alone is not enough to visualise the pore space, and other methods are needed to image pores in order to acquire transport properties. Other stones have so-called dual-porosity pore size distributions, meaning that there are larger pores connected by very fine connections. For these stones, dual pore network models (D-PNM) have been developed (Bultreys et al., 2015). In these models, extra connections representing the microporosity have been added to traditional PNMs in order to account for this microporosity. Although good results have been booked by fitting microporosity contributions to experimental data, these models could be improved by high-resolution, 3D data.

0.3 Image-based characterisation

In order to tackle the multi-scale problem, several destructive and non-destructive characterisation techniques exist to obtain chemical and structural information about a material at different resolutions, from molecular scale to lab scale. In this work, this characterisation is

performed on 3D rock samples of about 25 μm up to 10 centimetre in size, where we obtain resolutions down to around 10 nm for the smallest samples and several tens of micrometre for the largest samples. The focus lies on image-based characterisation techniques, which are used to acquire images of the structure and composition of materials at the pore scale. These techniques are discussed in detail in chapters 1, 2 and 3. While in chapter 1 the most mature and traditional methods for characterisation of natural stone are discussed, chapter 2 focuses on 3D characterisation using micro-computed tomography. Since this method is the most important one, its description is dedicated a full chapter. Chapter 3 describes a few highly advanced and novel methods for 3D characterisation, some of which have been used for the first time on geological materials. Afterwards, the acquired images are analysed using dedicated image analysis software, in order to perform quantitative measurements on the grain size, porosity and morphology of the pore network of the materials.

Terminology

To give additional background on image-based characterisation, images and image analysis, some terminology should be explained.

Images

In the case of image-based characterisation methods, images are basically raster files, where each raster box is called a *pixel*. Each image has to be acquired with a *detector* (in many cases this is called a *camera*, and normally each detection point in the detector raster will correspond to one pixel). However, several detector points can be *binned* together so that an average value of these points will correspond to a pixel. Pixels have one single value, which can represent a colour or a certain grey value. This value is a representation of a physical quantity (e.g. light intensity, X-ray attenuation, temperature, elemental concentration, etc.), and this quantity can be measured by the imaging technique or defined by a human operator. Pixels are usually squares, so they have the same dimensions in x and y, which is called the *pixel size*.

3D images

3D images are rasters of data-points, represented a virtual 3D volume, and are often stored as a stack of 2D images. These 3D datasets, as they are

called, have a certain pixel size in the x and y direction, but have an additional spacing between these images in the z direction. It is important to know that this z-spacing does not have to be the same as the pixel size.

Voxels

On element in a 3D image is called a *voxel*, which could be described as a 3D pixel. In the case of cubic voxels, where the z-spacing in a 3D dataset is the same as the pixel size, the size of one of the voxel edges is called the *voxel size*.

Spatial resolution

As mentioned above, perhaps the most important property of all of these imaging techniques is the spatial resolution they can obtain. This spatial resolution or resolving power can be defined as the smallest distance between two features in a sample, for which these features are seen as separate objects. It is worth mentioning that pixel/voxel size is often confused with spatial resolution. The latter is a measure for the resolving power of an imaging system based on the modulation transfer function (MTF) of the complete imaging system, expressed in line pairs per distance unit. Due to the complexity of the MTF, the term *resolution* is commonly used to denote the reconstructed voxel size, unless the spot size of the X-ray source is bigger. It must be noted that the term resolution can also denote the number of pixels or voxels in an image (Cnudde and Boone, 2013).

Microporosity

Several definitions for the term *microporosity* exist, including the approach by Sharkey and McCartney (1981), stating that all pores smaller than 2 nm are considered micropores, and pores larger than 50 nm are called macropores. When dealing with geological samples, however, even 50 nm pores are very small, and impossible to characterise with most imaging techniques. The term *microporosity* usually refers to pores that are too small to be analysed individually with a certain research technique. However, in most imaging techniques, sub-resolution porosity can still be noticed, usually by a grey value that lies between that of the solid matrix and real pores. This effect is known as the *partial volume effect* and will be explained in more detail in chapter 2.

Applied methods

Several image-based analysis methods are used in this work, and although the ultimate goal of this thesis is a full three-dimensional characterisation of a material, also 2D methods are used in this process. Perhaps the most important and mature method for non-destructive, structural 3D characterisation of geological materials is X-ray computed tomography (CT). Since we deal with high-resolutions in the micrometre ranges and we have an X-ray spot size of a few μm , we talk about micro-computed tomography (μCT , Cnudde and Boone (2013)).

Research into characterisation and visualisation of geological materials using μCT was jump-started by the petroleum industry, to study porosity and permeability of reservoir rocks. In this research field, the rapid development of micro- and nano-computed tomography resulted in a whole new research field called *digital rock physics*. Using this technique, the 3D structure of both consolidated and non-consolidated sediments could be imaged, accurate models of this structure could be produced and with the latest developments even fast, dynamic processes can be analysed in situ.

Besides in petroleum geology, μCT has become an invaluable tool for other fields in geology, such as sedimentology, mineralogy (Van Daele et al., 2014), hydrogeology (Wildenschild and Sheppard, 2013) and building stone research (Cnudde et al., 2006). Whereas μCT was considered an expensive method that was not readily available for researchers only a decade ago (Ketcham and Carlson, 2001; Øren and Bakke, 2002), the technique evolved so fast that nowadays (sub-) μCT has become available at many research centres around the world. Before the development of this method, 3D information on the pore and grain structure of stones was often based on descriptions of 2D thin section images. Based on statistical and process-based models, 3D models of a material could be built, allowing for the prediction of properties through modelling of various processes. A large disadvantage of these methods was that they do not allow to fully assess heterogeneous geomaterials. The availability of μCT systems created a way to directly image this heterogeneous structure at different resolutions and sample sizes. Due to the importance of μCT in this thesis, an entire chapter (chapter 2) is dedicated to the method.

Although the development of μ CT meant a huge leap forward in 3D imaging of materials, the method still has some flaws. Although it lends itself perfect for structural characterisation, μ CT provides only limited information on the chemical composition of the materials that are imaged. Therefore, data acquired from other methods needs to be combined with the μ CT data. These methods can simply be used to obtain more detailed information or information about different features, but can also be completely merged with the μ CT information. In this last case we talk about *data fusion*. The methods that are used here to fuse with μ CT data, can be seen as some very traditional geological methods, being optical microscopy and scanning electron microscopy (chapter 4). Besides these well-known methods, some recently developed high-end research methods will be implemented, being focused ion beam nanotomography and ptychographic tomography (chapter 5).

Using optical microscopy, geologists can determine the mineral composition of a stone, by examining thin sections. This method is probably the most standard and widespread for the characterisation of a stone's structure and composition. Experienced petrographers can identify the minerals that form the matrix of a rock, estimate the amount of pores and identify possible fossils. Features as small as around 500 nm can be seen using optical microscopy, but for many applications this resolution is still not high enough. In this case, higher resolution images are acquired using scanning electron microscopy (SEM), where the resolution limit lies around a few nanometres. Electron microscopes are often equipped with an energy-dispersive X-ray spectroscopy (EDS) detector, enabling chemical analysis of the investigated sample. Unfortunately, both of these analysis methods provide 2D data, and information on connectivity usually has to be provided using statistical models. A detailed description on both optical and electron microscopy is provided in chapter 1.

Over the last ten years several new methods have been developed to acquire images with a resolution similar to SEM in 3D. In 2004, Holzer *et al.* presented focused ion beam nanotomography (FIB-nt), a combination of a traditional SEM with a focused ion beam, capable of providing very high resolution 3D datasets (Holzer *et al.*, 2004). Unfortunately, in this serial sectioning method, the area of the sample that is imaged gets destroyed and is no longer available for future analysis. Non-destructive imaging at similar resolutions can be performed using ptychographic tomography (Dierolf *et al.*, 2010). Although these high-resolution data

provide a certain degree of chemical information besides the sample's microstructure, these samples have to be extremely small ($<100\text{ }\mu\text{m}$) and the method has limited availability and high operating costs. More information on these high-end research methods is provided in chapter 3.

0.4 Approach

The experiments and analyses in this thesis are performed on three sandstones with varying degrees of complexity: the German Bentheim sandstone, the French Vosges sandstone and the Indian Kandla Grey sandstone. Bentheim sandstone serves as a first test-material, as this sandstone is very homogeneous and has a low complexity in both structure and mineralogy. Its large grain size and well connected pore system make this stone relatively easy for 2D and 3D characterisation. The Vosges sandstone was selected as sample with higher complexity and proves to be more challenging to characterise. The stone consists of different mineral phases and the pore system is less connected than in Bentheim sandstone, and different pore sizes are present. Kandla Grey finally, is a very dense sandstone with a very low degree of porosity. These properties make Kandla Grey a rock that is hard to characterise using imaging techniques, since high resolution is needed in order to visualise its pore system. All of these stones have been or are used as building material and the first two served as analog for reservoir rocks. These three sandstones are discussed in chapter 1. In chapters 1, 2 and 3, the different characterisation techniques used in this thesis are thoroughly discussed, together with a review of their historic and recent applications on geological materials.

One of the approaches used in this work is the combination of μCT with classical microscopical techniques like optical microscopy and SEM-EDS. Next to the 3D structural information, emphasis will be put as well on the 3D geochemical composition. By combining SEM-EDS data and optical microscopy with μCT data, the obtained structural and chemical information will allow to characterise stones in a multi-disciplinary way as each technique provides complementary data to the specimen under investigation. The combination of SEM-EDS with μCT and optical microscopy techniques will largely contribute to process and mechanism characterisation as it will provide both chemical and structural information at the same time. Furthermore, since SEM-EDS and optical microscopy

are two-dimensional methods, mosaic imaging is able to provide images at high resolutions of surfaces with sizes in the centimetre range. This strengthens the 3D μ CT data by providing more details in the images and adding chemical information, enabling researchers to identify regions where more detailed information could be gathered by subsampling the material. A detailed example and workflow of this approach is demonstrated in chapter 4.

A next step is to push the limits in 3D resolution that traditional μ CT typically has. After carefully studying samples by using the highest possible resolution with μ CT and examining zones that are not resolved with other methods like optical and electron microscopy, interesting areas for subsampling can be identified and imaged in 3D at high resolutions. Therefore, experiments using FIB nanotomography and ptychographic tomography were performed, enabling the visualisation and analysis of the 3D structure of individual clay minerals and micas. Results of this section are presented in chapter 5.

In chapter 6 experiments are described that couple the analysed microstructure to the water management properties of the examined sandstones. Therefore, their pore network was extracted and the porosity and permeability was calculated based on this network and the acquired images. These results could be linked to real experiments performed in the laboratory. Later, chapter 7 shows the first results of the latest system of the UGCT and XMI, Herakles. This system combines high-resolution μ CT with X-ray fluorescence to enable direct 3D coupling of structure and elemental composition on a single sample. A detailed summary of the main conclusions and an outlook to future research is provided in chapter 8.

References

- M. J. Blunt, M. D. Jackson, M. Piri, and P. H. Valvatne. Detailed physics, predictive capabilities and macroscopic consequences for pore-network models of multiphase flow. *Advances in Water Resources*, 25:1069–1089, 2002. ISSN 03091708. doi: 10.1016/S0309-1708(02)00049-0.
- T. Bultreys, L. Van Hoorebeke, and V. Cnudde. Multi-scale, micro-computed tomography-based pore network models to simulate drainage in heterogeneous rocks. *Advances in Water Resources*, 78:36–49, apr 2015. ISSN 03091708. doi: 10.1016/j.advwatres.2015.02.003.
- V. Cnudde and M.N. Boone. High-resolution X-ray computed tomography in geosciences: A review of the current technology and applications. *Earth-Science Reviews*, 123(fufu):1–17, aug 2013. ISSN 00128252. doi: 10.1016/j.earscirev.2013.04.003.
- V. Cnudde, B. Masschaele, M. Dierick, J. Vlassenbroeck, L. Van Hoorebeke, and P. Jacobs. Recent progress in X-ray CT as a geosciences tool. *Applied Geochemistry*, 21(5):826–832, 2006. doi: DOI10.1016/j.apgeochem.2006.02.010.
- V. Cnudde, W. De Boever, J. Dewanckele, T. De Kock, M. Boone, M.N. Boone, G Silversmit, L. Vincze, E Van Ranst, H Derluyn, S Peetermans, J Hovind, P Modregger, M Stampanoni, K De Buysser, and G De Schutter. Multi-disciplinary characterization and monitoring of sandstone (Kandla Grey) under different external conditions. *Quarterly Journal of engineering Geology and Hydrogeology*, 46:95–106, 2013. doi: 10.1144/qjegh2012-005.
- M. Dierolf, A. Menzel, P. Thibault, P. Schneider, C. M. Kewish, R. Wepf, O. Bunk, and Franz Pfeiffer. Ptychographic X-ray computed tomography at the nanoscale. *Nature*, 467(7314):436–9, sep 2010. ISSN 1476-4687. doi: 10.1038/nature09419.

- R. H. Jr. Dott. Wacke, Graywacke and Matrix—What Approach to Immature Sandstone Classification? *Journal of Sedimentary Research*, 34(3):625–632, 1964. ISSN 1527-1404. doi: 10.1306/74D71109-2B21-11D7-8648000102C1865D.
- J. Gutiérrez, A. Mas, E. Gil, and V. Galvañ. Clay-related damage in rainscreen walls built with natural stone coverings. *Construction and Building Materials*, 29:357–367, 2012. ISSN 09500618. doi: 10.1016/j.conbuildmat.2011.10.060.
- L. Holzer, F. Indutnyi, P. H. Gasser, B. Münch, and M. Wegmann. Three-dimensional analysis of porous BaTiO₃ ceramics using FIB nanotomography. *Journal of microscopy*, 216(Pt 1):84–95, oct 2004. ISSN 0022-2720. doi: 10.1111/j.0022-2720.2004.01397.x.
- B. Jamtveit. *Fluid flow and transport in rocks*. Springer Science & Business Media, 1997.
- R. A. Ketcham and W. D. Carlson. Acquisition, optimization and interpretation of X-ray computed tomographic imagery: applications to the geosciences. *Computers & Geosciences*, 27(4):381–400, 2001.
- J. Maximilian Köhne, Steffen Schlüter, and Hans-Jörg Vogel. Predicting Solute Transport in Structured Soil Using Pore Network Models. *Vadose Zone Journal*, 10(3):1082, aug 2011. ISSN 1539-1663. doi: 10.2136/vzj2010.0158.
- Gary Nichols. *Sedimentology and Stratigraphy*, volume 20. 2009. ISBN 9781405193795.
- P. E. Øren and S. Bakke. Process based reconstruction of sandstones and prediction of transport properties. *Transport in Porous Media*, 46(2-3): 311–343, 2002.
- F. J. Pettijohn, P. E. Potter, and R. Siever. *Sand and Sandstone*. Springer US, New York, NY, 1973. ISBN 978-0-387-90071-1. doi: 10.1007/978-1-4615-9974-6.
- J. Ruedrich, T. Bartelsen, R. Dohrmann, and S. Siegesmund. Moisture expansion as a deterioration factor for sandstone used in buildings. *Environmental Earth Sciences*, 63(7):1545–1564, 2011. ISSN 18666280. doi: 10.1007/s12665-010-0767-0.
- E. Sebastián, G. Cultrone, D. Benavente, L. Linares Fernandez, K. Elert,

- and C. Rodriguez-Navarro. Swelling damage in clay-rich sandstones used in the church of San Mateo in Tarifa (Spain). *Journal of Cultural Heritage*, 9(1):66–76, 2008. ISSN 12962074. doi: 10.1016/j.culher.2007.09.002.
- A.G. Sharkey and J.T. McCartney. *Chemistry of Coal Utilization: Second Supplementary Volume*. Wiley, New York, 1981.
- M.E. Tucker. *Sedimentary Petrology: an introduction to the origing of sedimentary rocks*. Blackwell Scientific Publications, Oxford, 2nd edition, 1981.
- M. Van Daele, V. Cnudde, P. Duyck, M. Pino, R. Urrutia, and M. De Batist. Multidirectional, synchronously-triggered seismo-turbidites and debrites revealed by X-ray computed tomography (CT). *Sedimentology*, 61(4): 861–880, 2014. ISSN 13653091. doi: 10.1111/sed.12070.
- T. P. Wangler, A. Stratulat, P. Duffus, J. H. Prévost, and G. W. Scherer. Flaw propagation and buckling in clay-bearing sandstones. *Environmental Earth Sciences*, 63(7):1565–1572, 2011. ISSN 18666280. doi: 10.1007/s12665-010-0732-y.
- T. Weiss, S. Siegesmund, D. Kirchner, and J. Sippel. Insolation weathering and hygric dilatation: two competitive factors in stone degradation. *Environmental Geology*, 46(3-4), aug 2004. ISSN 0943-0105. doi: 10.1007/s00254-004-1041-0.
- D. Wildenschild and A. P. Sheppard. X-ray imaging and analysis techniques for quantifying pore-scale structure and processes in subsurface porous medium systems. *Advances in Water Resources*, 51(0):217–246, 2013. ISSN 0309-1708. doi: <http://dx.doi.org/10.1016/j.advwatres.2012.07.018>.
- E. M. Winkler. Frost damage to stone and concrete: geological considerations. *Engineering Geology*, 2(5):315–323, 1968.

1

Traditional characterisation methods and materials

The first section of this chapter describes the traditional characterisation methods for natural stones used in this thesis, to examine a stone's structure, chemical composition and behaviour. This chapter is limited to the methods that are used in this thesis. Additionally, this chapter will discuss the main three main sandstones studied in this thesis: Bentheim, Vosges and Kandla Grey sandstones. All of these materials are used as building stone, and have varying degrees of complexity. Going from the very simple Bentheim sandstone, over the chemically and structurally more complex Vosges sandstone, to the low-porosity Kandla Grey sandstone. For each material, the geological setting will be discussed, a petrographic description will be given, and the most important petrophysical properties of the material will be listed.

1.1 Traditional characterisation methods

This section has been included in an invited review that has been submitted to Earth Science Reviews as: *Imaging and image-based fluid transport modeling at the pore scale in geological materials: a practical introduction to the current state-of-the-art*. Bultreys, T., **De Boever, W.** and Cnudde, V. The Ph.D. candidate was responsible for this part of this review.

1.1.1 Optical microscopy

1.1.1.1 Traditional petrographic microscopy

The most widespread and standard method for the determination of the porosity and visualisation of the pore space of geological material is thin section analysis using an optical microscope (figure 1.1). The main advantage of this technique is that it is fast, cheap and widely accessible. Analysis of standard geological thin sections with a thickness of 30 μm under a petrographic microscope (figure 1.2) provides valuable information about both the mineralogical composition and structure of rocks and soils. High-end light microscopes are limited in resolution to about half the wavelength of light, known as the diffraction barrier. This means that at best, resolutions of about 0.23 μm can be achieved (Gustafsson, 2000; Heintzmann and Ficz, 2006). Petrographic microscopy can be used to analyse the porosity of geological materials, since pores appear transparent (white) in planar polarised light (PPL) and black under cross-polarised light (XPL) (Andriani and Walsh, 2002; Ingham, 2013). Since this may have overlap with isotropic minerals present (e.g.: fluorite, garnet), embedding samples with a blue coloured dye before thin section manufacturing, can help analysis significantly (Zhang et al., 2009). Optical microscopy images that are used for analysis are typically full colour images, as opposed to the grey scale images that are produced by many other techniques.

1.1.1.2 Fluorescence light microscopy

Fluorescence light microscopy (FLM) can be used for more exact characterisation of the pore space, since porosity and other components of

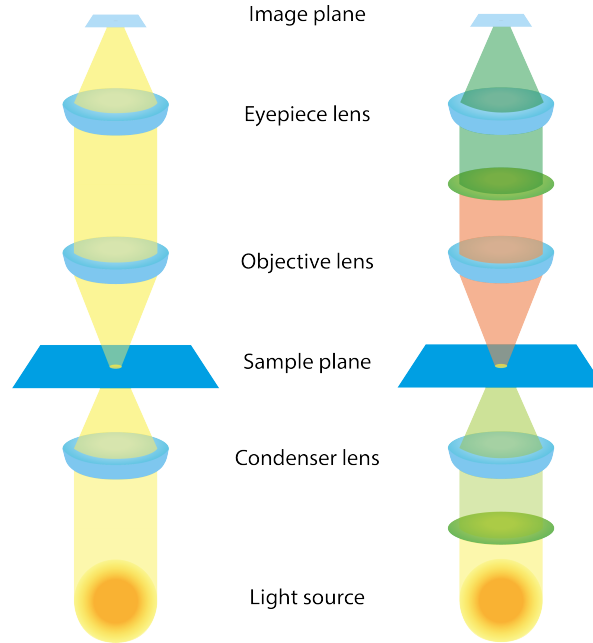


Figure 1.1: Schematic representation of the principle of traditional optical microscopy (left) and fluorescence light microscopy (right). Light travels from the light source through a condenser lens and hits the sample plane. An objective lens and eyepiece lens enable magnification. In fluorescence mode, an excitation and emission filter enable detection of the correct wavelengths for fluorescence imaging.

geological samples can be hard to distinguish from each other using classical optical microscopy (figure 1.2, left and center), both in planar and double polarised light (Nishiyama and Kusuda, 1994; Wajima et al., 2000). In FLM, samples are embedded with a fluorescent resin; when illuminated with light of correct wavelength, this fluorescent dye emits characteristic light, which provides a very clear contrast between material (black) and porosity (bright) (Ammouche et al., 2001; Sousa et al., 2005) (figure 1.2, right). This makes this technique very useful for the study of pores and (micro)cracks in rocks and concrete (Bisschop and van Mier, 2002; Jacobsen et al., 1995; Matějčíček et al., 2006; Poulikakos and Partl, 2010) and examine porosity in very low-porosity materials (Cnudde et al., 2012; Malaga-Starzec et al., 2006; Rivas et al., 2003). Furthermore, the sharp contrast between solid and void, makes it possible to use automated image analysis techniques to determine porosity on samples (Soroushian

et al., 2003). The technique requires that great care has to be taken in the preparation of the samples, since improper sample preparation can lead to false conclusions, e.g. over- or underestimation of porosity or crack density (Bisschop and van Mier, 2002; Soroushian et al., 2003).

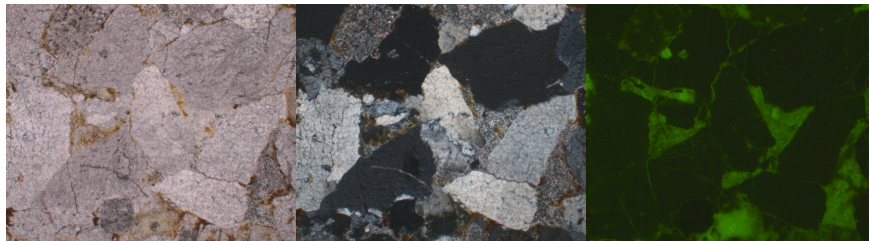


Figure 1.2: Example of a thin section (Baumberger sandstone) under traditional petrographic microscopy using parallel polarised light (left), cross-polarised light (center) and fluorescence light microscopy (right).

Zones of intermediate fluorescence intensity are an indication of pores with a size that is smaller than the resolving power of the microscope. The intensity of these zones depends on the degree of microporosity, where brighter zones are more porous than darker ones. This way, porosity that is invisible in traditional transmitted light microscopy can be observed (Leith et al., 1996). However, this technique is not adequate enough to thoroughly characterise the pore shape, connectivity and other properties of microporous materials, especially since it is a 2D analysis technique (Anselmetti et al., 1998). Nevertheless, FLM has been widely accepted in concrete research, where fluorescence intensity is used to determine water / cement ratio of the concrete, which stands in direct relationship with the capillary porosity of the concrete paste (Gran, 1995; Neville, 2003). The combination of a fluorescent dye and structured illumination microscopy can boost the resolution of optical microscopy up to a factor two (Gustafsson, 2000). More recent algorithms, which combine over 100 images into one single reconstructed plane can even go down to 50 nm resolution (Heintzmann and Ficz, 2006; Rego et al., 2012), however, this technique is very time-consuming and not yet used on geological samples.

1.1.2 Scanning electron microscopy

1.1.2.1 Introduction

2D imaging at higher resolution, going down to a few nanometres, can be obtained with scanning electron microscopy (SEM). With SEM, high-resolution images of both the minerals and the pore space in 2D can be obtained. SEM machines equipped with an energy-dispersive X-ray spectroscopy (EDS) unit can provide chemical information and, with correct calibrations and software even perform automated mineralogy (Hoal et al., 2009; Sutherland, 2007). SEM is a close relative of the electron microprobe (EMP) but is designed primarily for imaging rather than analysis. Images are produced by scanning the beam while displaying the signal from an electron detector on a TV screen or computer monitor. By choosing the appropriate detection mode, either topographic or compositional contrast (= mean atomic number) can be obtained. Since EMP instruments have electron-imaging capabilities, used primarily for locating points for analysis, the functions of the EMP and the SEM overlap considerably. The SEM is optimized for imaging, with analysis often as an extra, whereas in the EMP the priorities are reversed and various additional features that facilitate analysis are incorporated. The advantages of the SEM as an imaging instrument make it an invaluable tool in many branches of geology, including paleontology (SEM is ideally suited to the study of fossil morphology, especially that of micro-fossils), sedimentology (data on fabric and porosity can be generated as well as images of individual grains and intergrowths), mineralogy (to study crystal morphology on a micro-scale), etc.

In SEM, a high-energy electron beam scans the surface of the analysed samples (figure 1.3). These electrons interact with the atoms of the sample, producing signals that contain information about the samples topography and composition. These signals include secondary electrons, backscattered electrons, characteristic X-rays and cathodoluminescence. For the analysis of porosity inside a sample, the first two signals are most useful. One important disadvantage for SEM on geological materials is the fact that the samples often need some preliminary treatment. Most geological samples, being non-conductors of electric current, require a conductive coating to prevent charging under electron bombardment unless this is avoided by using an environmental or low-vacuum SEM. The preferred coating element for X-ray analysis is carbon, because it has a

minimal effect on the X-ray spectrum (Reed, 2005). It is also the best choice for cathodoluminescence studies. However, for SEM imaging, owing to its low secondary-electron yield, it is not ideal. For this purpose a metal such as gold is preferable, but less suitable for X-ray analysis and BSE imaging.

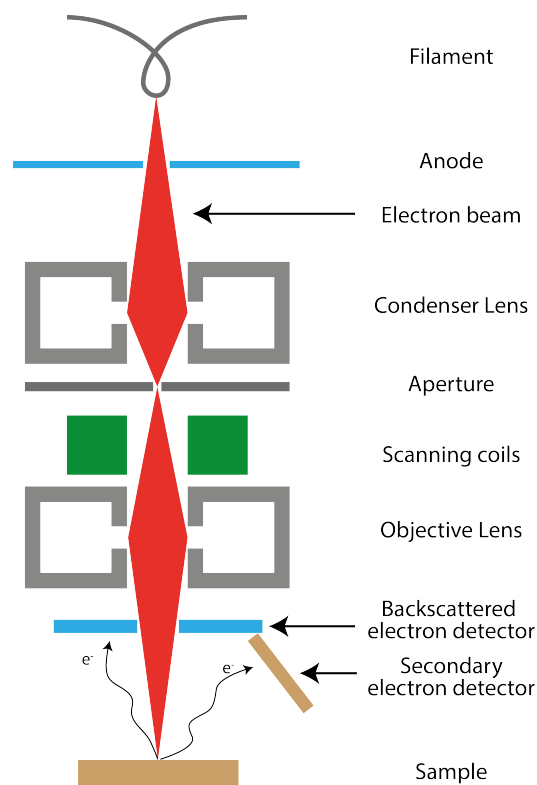


Figure 1.3: Schematic representation of the electron beam in a SEM.

1.1.2.2 Analysis

Imaging

The types of signals produced by a SEM include secondary electrons (SE), back-scattered electrons (BSE), characteristic X-rays and cathodoluminescence (figure 1.4). Secondary electrons (SE) are produced when an incident electron excites an electron in the sample. This excited electron moves towards the surface of the sample, where they can escape

the sample, and reach the detector. Secondary electrons can only escape the sample if they are formed within 1 nm of the sample surface, and typically have very low energies (up to 50 eV). Due to their very small production volume, resolution of secondary electron images (SEI) is very high, and is effectively the same as the electron beam size, which is normally below 10 nm. SEMs equipped with a Field Emission electron gun (FE-SEM) can even reach beam sizes of about 1 nm. Another effect of this very small interaction volume is that SE are very sensitive to sample topography, making SE images very useful to study this property of a material (Reed, 2005). The very high resolution of SE images makes them very suited for analysis of microstructures and (micro)porosity in various fields of geosciences, such as oil and gas (Huang et al., 2013; Jiao et al., 2014), concrete research and soil science.

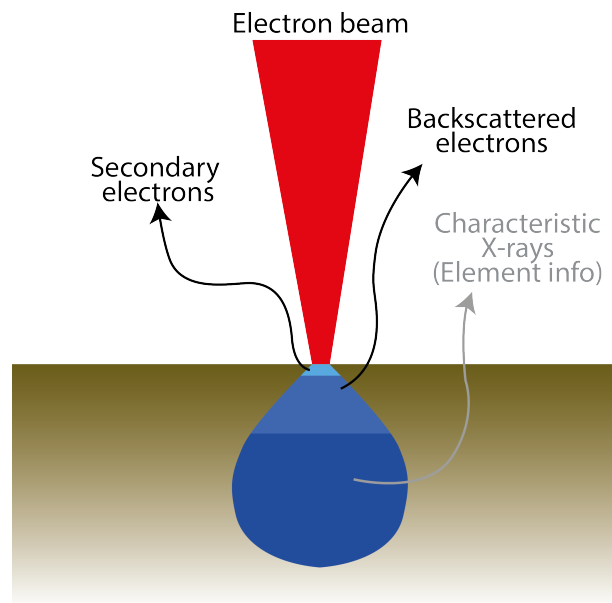


Figure 1.4: Electron beam-specimen interactions. Secondary electrons originate from a region close to the sample surface (5 nm), Backscattered electrons originate up to 500 nm deep, and characteristic X-rays can originate about 2 μm below the sample surface.

Backscattered electrons (BSE) are electrons that originate from the beam, but reflect from the sample by elastic scattering. Most BSE have quite slightly lower energy than that of the incident electron beam, but energies

as low as ± 50 eV are possible. Since the fraction of beam electrons that is backscattered strongly depends on the average atomic number of the sample (higher Z causes more backscattering, due to higher charge of atomic nuclei), BSE images provide information about a samples composition (figure 1.5). Spatial resolution in BSE images is considerably lower than in SE images, due to the much larger interaction volume. Best spatial resolution is therefore reached by using a low accelerating voltage (Reed, 2005). Both SE and BSE images provide an intuitive 3D-like look, enabling researchers to look inside a pore (figure 1.5) for porosity analysis, polished thin sections are more valuable, as the difference between material and voids is more easily observed.

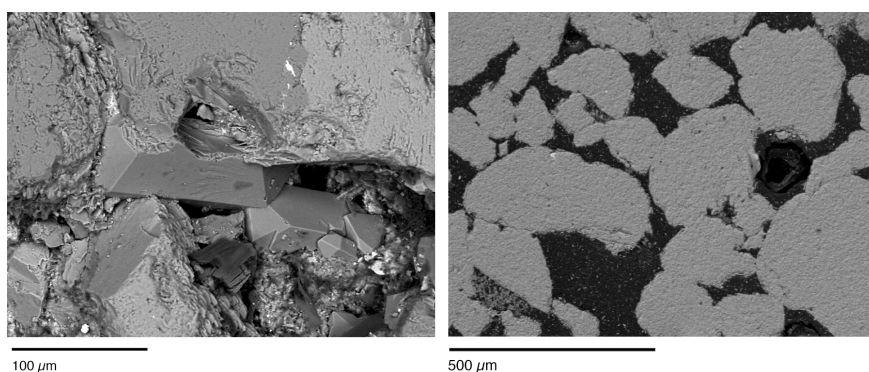


Figure 1.5: Left: BSE image of unpolished Vosges sandstone, showing primary quartz grains and secondary prismatic quartz crystals. The high working distance creates a 3D impression in the picture. Right: BSE image of a polished, resin embedded Bentheim sandstone sample. This type of image is ideal for 2D porosity determination.

JEOL JSM-5310LV

SEM images in this thesis were taken using the JEOL JSM-5310LV microscope of the PProGress and MinPet group (Dept. of Geology and Soil Science, Ghent University). This machine is a device from 1996 and can image in both secondary electron mode as backscattered electron mode. Due to the compositional contrast, most images in this work are backscattered electron images.

Chemical analysis

A side-effect of bombarding a sample with high-energy electrons is the production of X-rays by its constituting elements. These characteristic

X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy partly in the form of X-rays. The X-ray spectrum that each element produces is characteristic for the element's atomic structure, and therefore it can be used to uniquely identify the composition of a sample. A lot of SEMs are equipped with detectors to analyse the spectrum of these generated X-rays, in order to couple imaging capabilities with chemical analysis. X-ray analysis on SEMs and electron microprobes can be divided into two main methods: energy-dispersive X-ray spectroscopy (EDS) and wavelength-dispersive spectroscopy (WDS). The most important difference between both methods is that in EDS different elements are identified based on the difference in X-ray energy, whilst in WDS differences in X-ray wavelength are measured. Both methods are varieties of X-ray fluorescence spectroscopy. In practice, sodium ($Z=11$) is often the lightest element that can be detected, although newer systems can go down to beryllium ($Z=4$). Older systems have limited capabilities in semiquantitative analysis of sodium, therefore limiting to differentiate between minerals where the relative concentration of sodium is important, such as feldspars, micas and clay minerals (?).

Chemical analysis using the JEOL JSM-5310 LV

The JSM-5310LV is equipped with a liquid nitrogen-cooled SiLi energy-dispersive detector, manufactured by Oxford Instruments. Combined with the ISIS software package, this system can perform point analyses, line scans and elemental mappings. Since the maximum accelerating voltage of the system is 30 kV, reliable analysis can be performed up to a $K\alpha$ value of 15 keV, making Y the heaviest element that's inside this analysis range. However, the L or M peaks of heavier elements can lie inside the observable interval.

1.1.3 Applications

SEM is a widely accessible, and therefore a very frequently used technique in geology, starting very soon after the first commercial machines became available in the 1960s. Earliest implementations of the method were for the characterisation of natural stones and minerals. SEM was used as a tool to study pore systems (Timur et al., 1971) and the morphology of limestone as early as 1971 (Margolis and Rex, 1971). A decent review of the use of BSE images to distinguish different mineral

phases has been made by Lloyd (1987). Besides that, SEM was used for the investigation of important geological processes, such as diagenesis and weathering. Longman and Mench (1978) used the technique to study the diagenesis of cretaceous limestone, whilst others used it to study different types of very fine-grained clay minerals, formed by the weathering of feldspars (Keller, 1978). In the 1980s, automated procedures were developed to characterise stone microstructure automatically, laying the foundations of current image analysis procedures (Krohn and Thompson, 1986). Later, SEMs were used in reservoir geology, for the investigation of nano-porous cap rocks, tight shales (Katsube and Williamson, 1994) and clay minerals (Hillier, 1994).

1.1.4 Petrophysical characterisation tests

The term *petrophysical characterisation tests* refers to traditional laboratory test to determine the petrophysical properties of natural stone. In most cases, these tests are performed following official European standards, and for most stones, there exist technical data sheets listing these properties. Several of these tests are of importance for this thesis and are discussed here. These tests include the determination of the open porosity, determination of the apparent density, determination of the capillary absorption coefficient and mercury intrusion porosimetry.

Determination of the open porosity and apparent density

The simplest way to determine the open porosity of a stone is by saturating the stone with water under vacuum, in this case following the European standard *EN 1936 (2006): Natural stone test methods Determination of real density and apparent density and of total and open porosity*. In this method, oven dried samples are saturated with water under a vacuum, and weighted under water and in air. By combining dry weight (m_d) and both saturated weights (m_s : above water, m_h : under water) of the sample, open porosity can be determined by equation 1.1.

$$p_0 = \frac{m_s - m_d}{m_s - m_h} \cdot 100(\text{vol.}\%) \quad (1.1)$$

Although this is a cheap and fast technique to measure the porosity of a stone, it tells us nothing about size and distribution of the pores. Using the

same method, the apparent density of natural stones ρ_b can be determined, this time using a different formula.

$$\rho_b = \frac{m_d}{m_s - m_h} \cdot \rho_{rh} \quad (1.2)$$

In this formula, ρ_{rh} is the density of water at 20°C, determined at 998 kg/m³.

Capillary absorption coefficient

The capillary absorption coefficient (C) of a natural stone is a measure of how fast a stone absorbs water by capillary forces. This test is performed according to European standard *EN 1925 (1999): Natural stone test methods - determination of water absorption coefficient by capillarity*. In this test, samples are placed in 3 ± 1 mm of water, and the evolution of their weight is measured over time. Typically, when plotted over the square root of time, this weight evolution follows a linear path in the beginning, before leveling out onto a plateau (figure 1.6). The capillary absorption coefficient can be determined by measuring the slope of the first part of this figure, corresponding to equation 1.6, where m_i and m_d represent the weight of the sample at time i and its dry weight respectively.

$$C = \frac{m_i - m_d}{A \cdot \sqrt{t_i}} \quad (1.3)$$

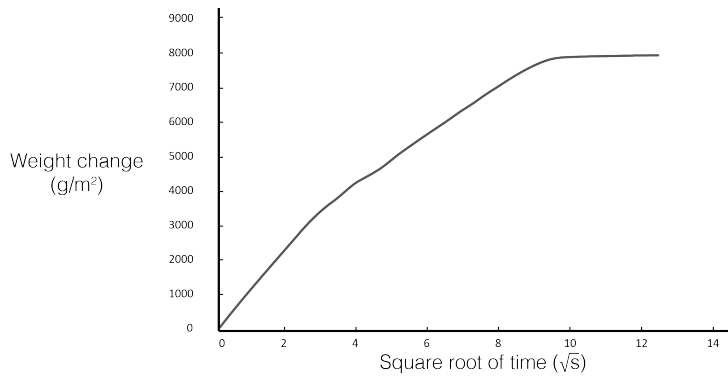


Figure 1.6: Capillary absorption graph measured on the Bentheim sandstone. The capillary absorption coefficient is determined by the slope of the left part of the graph.

1.1.5 Mineralogical analysis using X-ray diffraction

X-ray diffraction (XRD) is an analytical technique primarily used for phase identification of a crystalline material and can provide qualitative information on unit cell dimensions. X-ray diffraction is based on constructive interference of monochromatic X-rays in a crystalline sample due to the periodicity in the sample. These X-rays are generated by an X-ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law (equation 1.4).

$$n\lambda = 2d\sin\theta \quad (1.4)$$

This law relates the wavelength of electromagnetic radiation to the diffraction angle θ and the spacing between crystallographic planes in a crystalline sample (d). These diffracted X-rays are then detected, processed and counted. Conversion of the diffraction peaks to d -spacings allows identification of the mineral because each mineral has a set of unique d -spacings. Typically, this is achieved by comparison of d -spacings with standard reference patterns. XRD patterns of powdered samples of material were collected with a Philips X'pert System (CuK α radiation, scan time 1 s per 0.02° 2 θ).

1.2 Materials

In this section, the three most important sandstones used in this thesis are described. These sandstones are all used as building materials in Western-Europe, and were selected based on their composition and structure. Bentheim sandstone is a very pure sandstone, with large grain size and straight-forward pore system. The rock has a low amount of cement, is very homogeneous and has been well described in literature. Therefore, Bentheim sandstone is an excellent material for first experiments and development of methods. The Vosges sandstone was selected based on its higher complexity, both in terms of structure and composition. The Vosges sandstone has a smaller grain size, broader pore size distribution and less connected pore network than the Bentheim

sandstone. Kandla Grey, finally, is a dense rock, with a very low porosity and close packing. These properties make it a very challenging material to characterise using image-based analysis methods.

1.2.1 Bentheim sandstone

The Bentheim sandstone is a German sandstone of Early-Cretaceous (Valanginian, 125 Ma) age. This rock is both an important building material (especially in the Netherlands), a frequently used test sample in fluid flow related studies (Ramstad et al., 2012; Klein and Reuschle, 2003) and an analogue for reservoir rock (Ojala, 2011) modeling. The Bentheim sandstone is also the host rock for the Dutch *Schoonebeekveld* reservoir. It is a fine to medium grained sandstone, and can be classified as a quartz arenite. The grain size varies between 100 and 500 μm . The fine, homogeneously spread pores give the rock a high porosity and permeability (Dusar et al., 2009). Combined with its simple structure, this makes it an excellent reservoir analog in fluid flow studies (Dubelaar and Nijland, 2015b; Olafuyi et al., 2010; Ramstad et al., 2012). The uniform outlook and high frost resistance make it very suitable as a building stone, and buildings were built in Bentheim sandstone as early as 1000 A.D. (Dubelaar and Nijland, 2015a). The surface of the stone typically turns black by biological weathering (Nijland et al., 2003a). The stone was mainly used in Germany and the Netherlands and the northern part of Belgium.

Geological setting macroscopical appearance

The Bentheim sandstone outcrops between the towns of Bad Bentheim and Gildehaus in western Germany (figures 1.8 and 1.7). It is found in the Lower-Cretaceous layers of the Valanginian, with a maximum thickness of up to 80 metres. In the lower Valanginian, three transgressive-regressive cycles can be distinguished (figure 1.9) in which the rock can be found as massive or cross-bedded layers (Dubelaar and Nijland, 2015b). The sandstone package was deposited in the western part of the Lower Saxony Basin, close to the Dutch border, in shallow marine environment. The main outcrop is a 8 to 9 km long east-west aligned ridge, approximately 400 metres wide (Dubelaar and Nijland, 2015b). This ridge is part of an anticline formed during the Alpine orogenesis and stretches from the town of Gildehaus in the west to Suddendorf in the east. In the western part, the rock is found in a pale greyish to yellow variety, called the Gildehaus

variety. Around the town of Bad Bentheim and further east, the stone is found in an ochre to even red variety, called the Bentheim variety. The type section of the stone was established in the Romberg quarry in Gildehaus, which is the only active quarry of Bentheim sandstone, and is also the origin of the samples used in this thesis. Samples of the Bentheim variety of the sandstone originated from a quarry below the parking space of the Bad Bentheim open air theatre, just east from the city centre. This quarry is reopened every four years, if there is a demand for new samples.

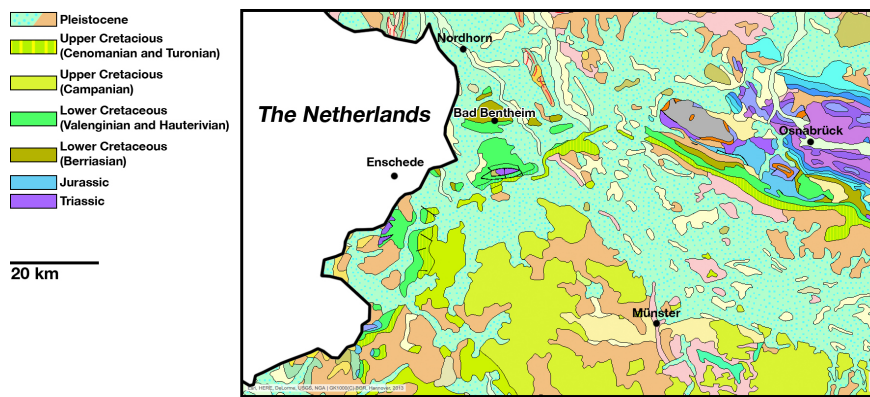


Figure 1.7: Geological map of a part of Western-Germany, including Bad Bentheim. Source: German Geological Survey

Petrographical analysis

The Gildehaus variety of the Bentheim sandstone consists of well-sorted medium-grained sands, with an average grain size between 180 and 300 μm , although grains of up to 500 μm occur (figure 1.10). 90 to 95 % of the rock consists of quartz, and feldspars such as microcline and plagioclase are rare, hence the material is classified as a quartz arenite according to Pettijon (Pettijohn et al., 1973). Accessory heavy minerals such as zircon and tourmaline and iron-hydroxides and oxides such as goethite and hematite occur in the stone. Clay minerals are rare in the stone, but a small amount of kaolinite can be found in some locations of the stone's structure. The material has a very high porosity which can be measured to be up to 30 percent in fluorescence microscopy images (figure 1.11). The Bentheim variety of Bentheim sandstone gets its characteristic red colour by the presence of hematite (Fe_2O_3), which coats the quartz grains and fills a significant part of the pore space. A clearly higher concentration of fine-grained minerals is present these stones, and in the

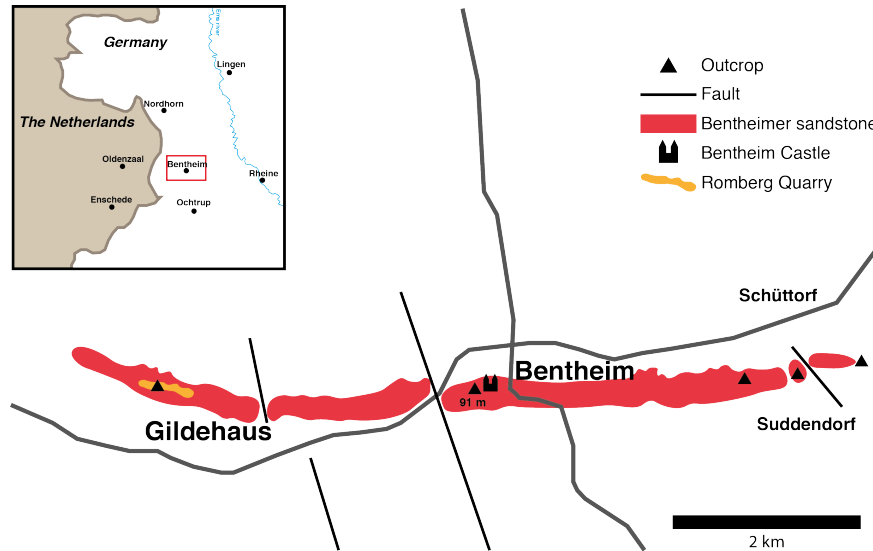


Figure 1.8: Appearance, outcrops and quarry of the Benthheim sandstone. After Nijland et al. (2003b).

Stage	Ammonite zones	Micropal. zonation	Lithostratigraphy	Type locality (Romberg)	Sequence stratigraphy
VALANGINIAN	<i>Eleniceras paucinodeum</i>	OV 3+4	clay		
	<i>Dicostella tuberculata</i>				
	<i>Prodichotomites ivanovi</i>				
	<i>Dichotomites bidichotomoides</i>				
	<i>Dichotomites triptychoides</i>	OV 2	<i>Dichotomites</i> Sandstone		
	<i>Dichotomites crassus</i>				
	<i>Prodichotomites polytomus</i>	OV 1	erectum Clay		
	<i>Prodichotomites hollwedensis</i>				
	<i>Polyptychites sphaeroidalis</i>	UV 2	Upper Benthheim Sandstone		FS Benthheim 3
	<i>Polyptychites clarkii</i>		Romberg Clay		FS
	<i>Polyptychites multicostatus</i>		Sudden-dorf Clay		Benthheim 2
	<i>Polyptychites paviowi</i>		Haupt Sandstone		FS Benthheim 1
			Heterolith. Facies		
			Basisbank		
			Lower bioturbated zone		
	<i>Platylenticeras involutum</i>	UV 1	<i>Platylenticeras</i> Clay	10 m	MFS
	<i>Platylenticeras heteropleurum</i>				
	<i>Platylenticeras robustum</i>				

Figure 1.9: Lithology, biogstratigraphy and sequence stratigraphy of the Valanginian in the Lower Saxony basin. From Stadler (1998).

analysed samples, the average grain size is slightly lower in this variety. Due to the higher amount of clay minerals, the presence of hematite and the smaller grain size, porosity of the Bentheim variety samples is significantly lower than in the Gildehaus variety. On photomicrographs (figures 1.12 and 1.13) it is clearly seen that the Bentheim variety has much denser packing than its westerly neighbour.

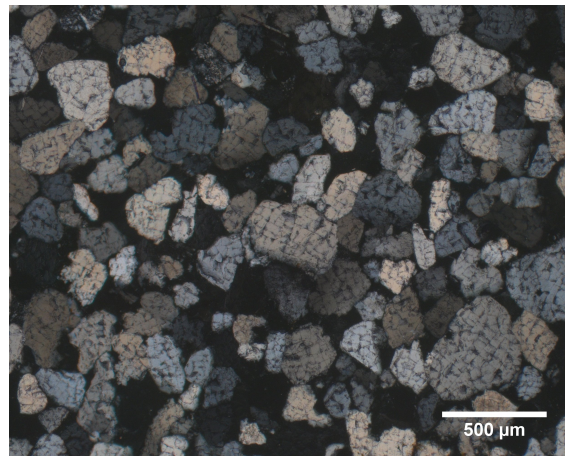


Figure 1.10: Photomicrograph of the Bentheim sandstone, Gildehaus variety, in XPL.

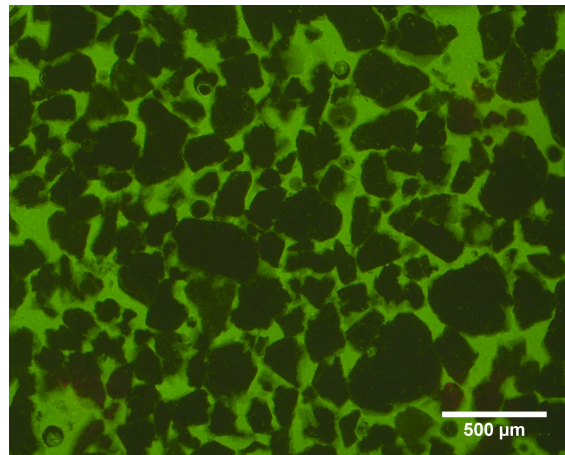


Figure 1.11: Fluorescence microscopy image of the Bentheim sandstone, Gildehaus variety. Pores appear bright green, whereas grains are black.

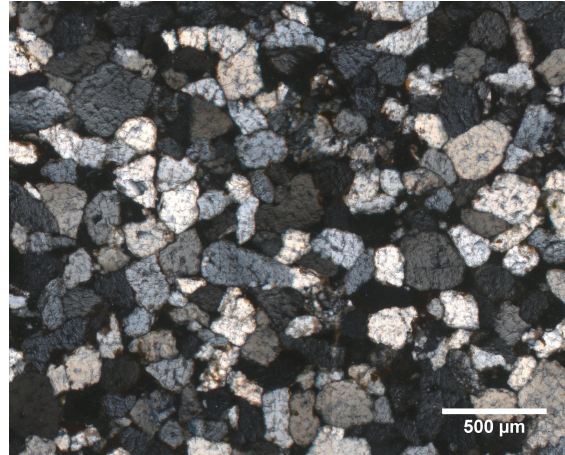


Figure 1.12: Photomicrograph of the Bentheim sandstone, Bentheim variety, in XPL.

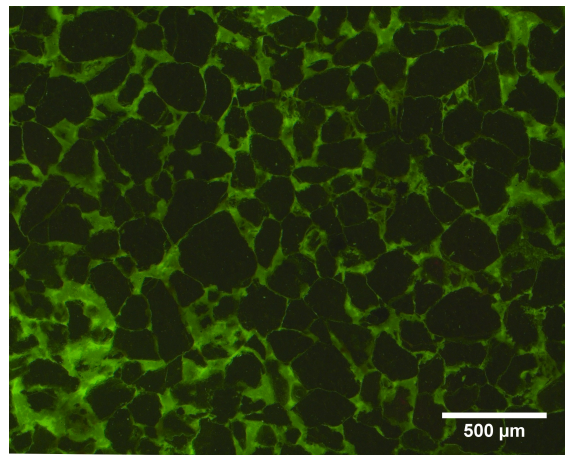


Figure 1.13: Fluorescence microscopy image of the Bentheim sandstone, Bentheim variety.

Using BSE images we can clearly see this packing difference between the Gildehaus and Bentheim variety (figure 1.14). Furthermore, it is possible to study the microstructure of the clay minerals that are situated between the grains of the stone (figure 1.15, both in the grey as the red variety of the stone). Using the EDS detector of the setup, these clay minerals were identified as kaolinite ($Al_2Si_2O_5(OH)_4$).

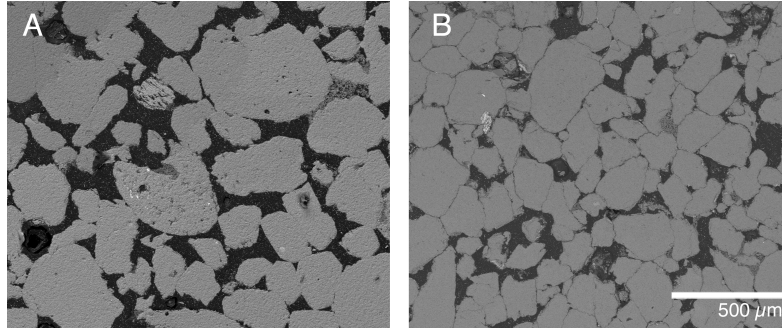


Figure 1.14: A: SEM image of the Gildehaus variety of Bentheimer sandstone. B: SEM image of the Bentheim variety of Bentheimer sandstone, with noticeable smaller grains and denser packing.

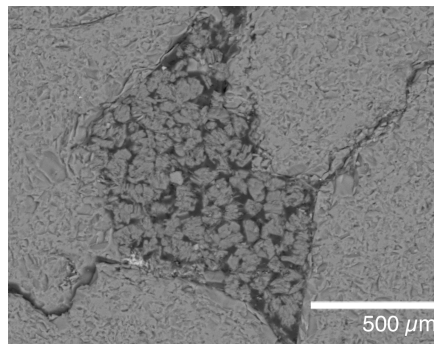


Figure 1.15: Detail from figure 1.14 B: Kaolinite fills some pores of the sandstone.

Characterisation tests

Bentheim sandstone is characterised by its very high porosity. Open porosity values measured by water absorption under vacuum reached an average of 22.50 vol.% for the Gildehaus variety and 18.50 vol.% for the Bentheim variety 1.1. The apparent densities lie around 2030 kg/m^3 for the Gildehaus variety and 2150 kg/m^3 for the Bentheim variety. Capillary water absorption of the Gildehaus variety is very fast, with values for C of $624 \text{ g.m}^{-2}.\text{s}^{-1/2}$. Due to denser packing and lower porosity, the absorption in the Bentheim variety tends to be a lot slower, with an average capillary absorption coefficient of around $44 \text{ g.m}^{-2}.\text{s}^{-1/2}$.

Material	Open porosity vol. %	Apparent density kg/m ³	C g.m ⁻² .s ^{-1/2}
<i>Bent. Gildehaus</i>	22.57 ± 0.07	2033 ± 1.9	624.0 ± 92.7
<i>Bent. Bentheim</i>	18.48 ± 0.18	2152 ± 5.5	44.5 ± 4.2
<i>Vosges sandstone</i>	21.14 ± 0.27	2094 ± 10	81.7 ± 9.2
<i>Kandla Grey</i>	3.02 ± 0.62	2683 ± 7.7	2.96 ± 0.42

Table 1.1: Open porosity determined by water absorption, apparent density and capillary water absorption coefficient *C* of different sandstones.

1.2.2 Vosges sandstone

The second material used in this thesis is a sandstone from the Vosges mountains in north-eastern France. The Vosges sandstone is more complex in terms of both composition and structure, compared to the Bentheim sandstone. The stone has been used as a building stone (e.g. in the cathedral of Strasbourg, Colas et al. (2011)) and has been used for fluid flow and mechanical strength simulations (Bésuelle et al., 2000; Schmitt et al., 1994; Charalampidou et al., 2011). In Germany, the stone is known as the Voltzien Sandstein.

Geological setting and macroscopical appearance

The specific name for this rock is Meule sandstone (*Grès à meules*), but during the majority of this work, it is referred to as Vosges sandstone. The Meule sandstone Formation forms the lower part of the *Grès à Voltzia*, which forms the upper part of the Buntsandstein facies, and is early Triassic (Anisian) in age (Shear et al., 2009). The facies in the Upper Buntsandstein are mainly fluvial deposits, consisting of medium to coarse sandstones (Bourquin and Durand, 2006). The *Grès à Voltzia* formation was deposited in a meandering river system, with a low degree of marine influence, and the deposits form the eastern-most boundary of the Paris Basin. The Meule sandstone is excavated at near the Lower- to Middle-Triassic boundary, e.g. in Niderviller (figures 1.16 and 1.17).

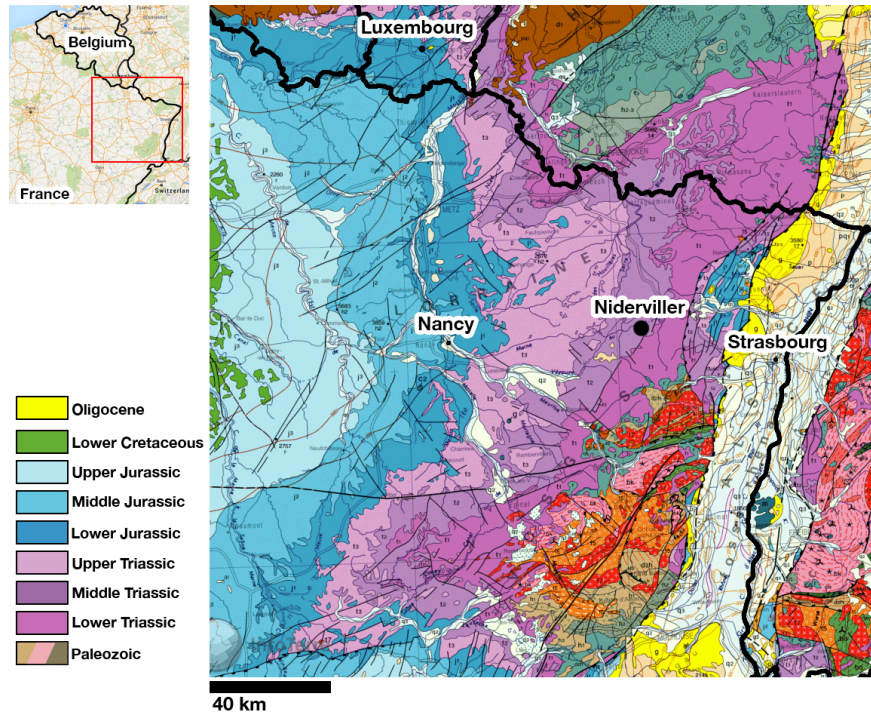


Figure 1.16: Geological map of Eastern France. The Meule sandstone is quarried near the Lower- to Middle-Triassic boundary. Source: French Geological Survey

The rock is a fine-grained red to pink sandstone, that contains up to 30 % of feldspars (Gall and Grauvogel-Stamm, 2005). Average grain size according to the literature is around 80 μm and between 3 and 15 % of the material consists of clay minerals such as illites, micas, kaolinite and smectites (Van Den Abeele et al., 2002; Thomachot and Jeannette, 2004; Schmitt et al., 1994).

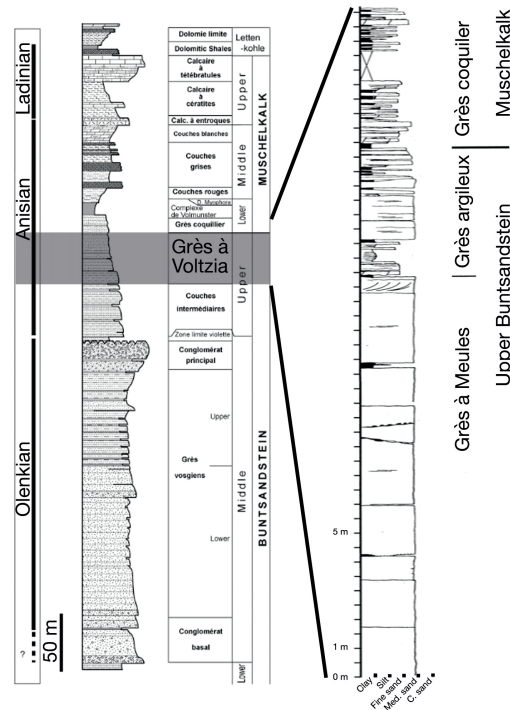


Figure 1.17: Stratigraphic location of the Middle and Upper Buntsandstein, with the Grs Voltzia Formation highlighted, the Grs Meules sandstone is situated inside this formation. The detailed lithographic column is acquired at the Metzger quarry in Niderviller (Fr.) (adapted from Bourquin and Durand (2006)).

Petrographical analysis

The Vosges sandstone primarily consists of quartz (50 - 60 %) and weathered feldspars (30 - 40 %), with an average grain size of around 100 μm , but the sorting of the grains is rather poor. Due to this mineral composition, the stone can be classified as an arkose (figure 1.18). Between the grains, iron oxides (red in PPL) are abundant, filling a large part of the porosity. Besides these iron oxides, fine-grained minerals are present, but the exact type cannot be determined using optical microscopy. Elongated phyllosilicates all carrying the same orientation parallel to the depositional plane of the stone are present. These minerals can easily be identified as muscovite and chlorite. Fluorescence microscopy reveals a rather high porosity, with a lot of sub-resolution microporosity in the pore-filling minerals (figure 1.19).

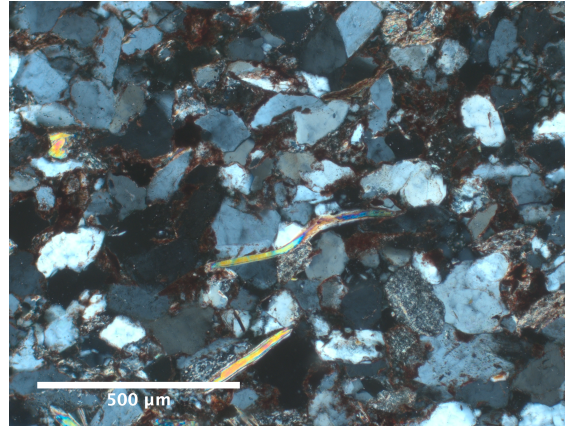


Figure 1.18: Photomicrograph of the Vosges sandstone in PPL. In the image, quartz, feldspars and micas are present.

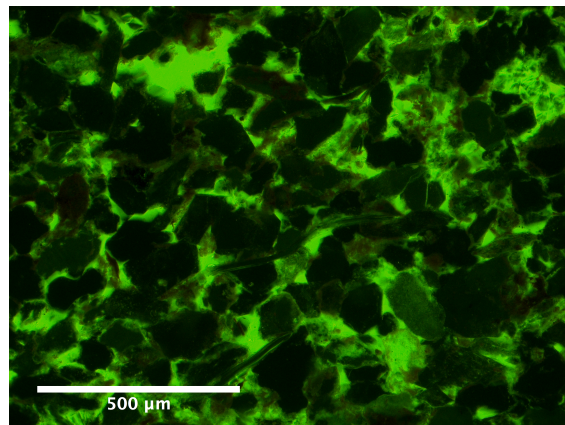


Figure 1.19: Fluorescence microscopy image of the Vosges sandstone.

BSE images from the Vosges sandstone (figure 1.20) clearly show the chemical and structural complexity of the material, compared to the Bentheim sandstone. The average grain size of the material is clearly smaller than in Bentheim sandstone and grains are much more angular, suggesting a less mature stone. The majority of the pores is filled with large and small clay mineral grains, and a lot of very fine, microporous matrix. EDS analysis of the pore-filling minerals resulted in different clay fractions. In figure 1.21, quartz appears grey, as these are the areas where only silicon is found. Areas where only aluminium is present are identified

as kaolinite clusters or smectites, and the difference between these two phases can be seen based on their structure. In mica minerals (muscovite and chlorite), both aluminium and potassium occur together. This is also the case in feldspars, but there the aluminium amount is much lower and gets overruled by the potassium signal. In the image, there is one big iron oxide grain present, the rest of the iron is present as a very thin layer coating the quartz grains.

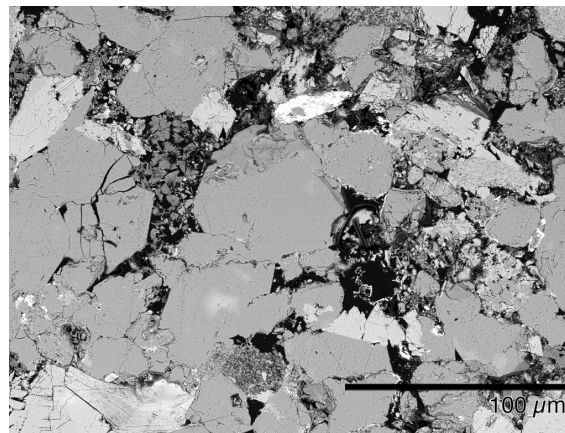


Figure 1.20: BSE image of Vosges sandstone.

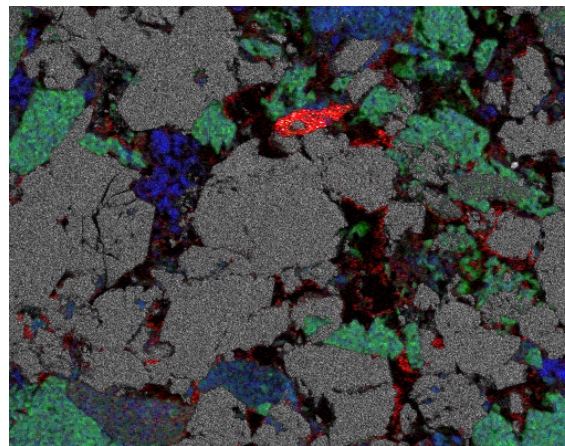


Figure 1.21: EDS maps for silicon (grey), potassium (green), aluminium (blue), iron (red) and titanium (yellow). Measurements were performed on the same area as figure 1.20.

Characterisation tests

The open porosity of the Vosges sandstone is also high, at 21 vol.%. Unlike the Bentheim sandstone, the stone does not have a very fast capillary water absorption coefficient, this value lies at $81 \text{ g.m}^{-2}.\text{s}^{-1/2}$. The apparent density of the Vosges sandstone averages at 2094 g/m^3 . The mineralogical composition was confirmed by powder X-ray diffraction, as the most important peaks in the pattern represent quartz, feldspars and micas.

1.2.3 Kandla Grey sandstone

Large parts of this section come from the publication "*Multi-disciplinary characterisation and monitoring of sandstone (Kandla Grey) under different external conditions.*" by Veerle Cnudde, **Wesley De Boever**, Jan Dewanckele, Tim De Kock, Marijn Boone, Matthieu Boone, Geert Silversmit, Laszlo Vincze, Erik Van Ranst, Hannelore Derluyn, Steven Peetermans, Jan Hovind, Peter Modregger, Marco Stampanoni, Klaartje De Buysser and Geert De Schutter, which was based on my master's thesis (Cnudde et al., 2013).

Kandla Grey is an Indian sandstone that is being quarried and imported into Western Europe on a massive scale, and mainly used as a pavement stone. Its low costs and high strength are the reason for its popularity, although there have been reported problems due to the mica minerals in its structure (Cnudde et al., 2013). The dense structure of the stone and low porosity make it a challenging material to image, and therefore it is an excellent material in methodological studies.

Geological setting and macroscopical appearance

Kandla Grey is an Indian compact sandstone found in east to south-east Rajasthan. It is a grey siliceous sandstone that can be classified as a subarkose according to Pettijohn (Pettijohn et al., 1973). The stone is excavated from the Vindhyan and Delhi Supergroups, which outcrops over an area of over 1 million square kilometres and has a cumulative thickness of over 4 kilometres. The age of the Vindhyan and Delhi supergroup deposits lies between 1600 and 650 Ma (Ray, 2006), Kandla Grey originates from the upper part of this time interval. The sandstone-producing districts in Rajasthan have been grouped into different mining clusters, each producing sandstone with certain

distinguishing features. Kandla Grey belongs to the Jaisalmer cluster, which is located at several places including Jaisalmer town, Bada Bagh, Hamira, Bedasar, Habur, Mokal, etc. In general these sandstones, including Kandla Grey, are fine grained and compact. Kandla Grey is the commercial name for quarried rocks with a grey colour, but physico-mechanical and chemical properties of the sandstone quarried from different areas in Rajasthan determine its quality, colour and use. Due to the enormous scale of the rock's exploitation, an exact origin of the stone is impossible to trace, and Kandla Grey is known under a wide range of commercial names (e.g. Autumn Grey, Budhpura Grey, Bhilwara Grey, Kota Grey, etc.) The rock contains dark laminations, both cross-bedded as parallel to the deposition plane, and has the characteristics of a beach deposit.

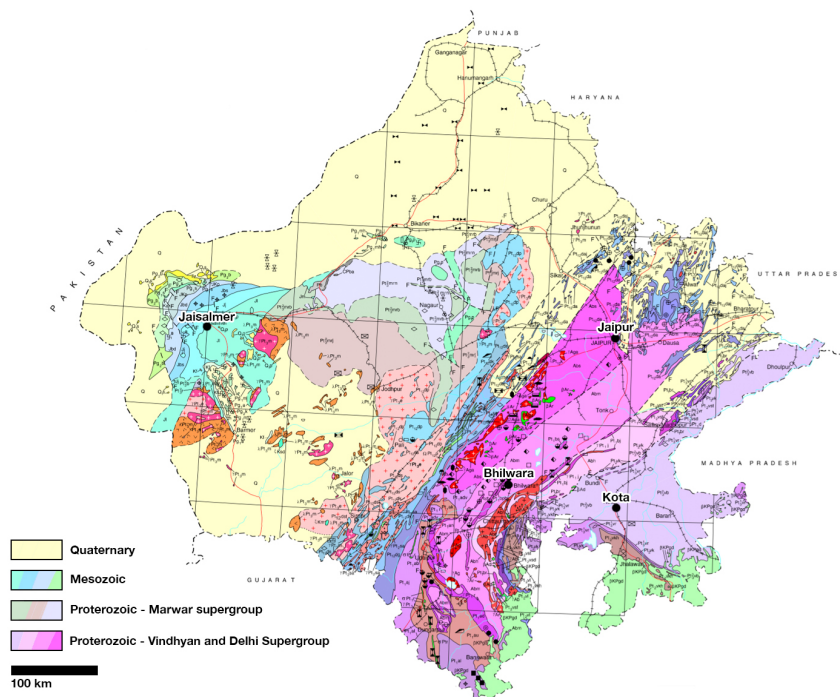


Figure 1.22: Geological map of the Rajasthan province in North-West India. Kandla Grey is found in the proterozoic layers of the Vindhyan and Delhi supergroup. Source: Indian Geological Survey

Petrographical analysis

Kandla Grey is a fine-grained subarkose consisting of about 80 % of quartz, 15 % of feldspars and about 5 % of accessory minerals such as micas, zircon and rutile. The average grain size of the mono-crystalline quartz grains is about 100 μm , and most grain contacts show pressure-solution effects due to the compaction of the stone (figure 1.23). The mica minerals are oriented parallel to the sedimentary layering of the stone, with an irregular spacing between them. The dark laminations correspond to alignment of dark brown minerals, that are too small to be identified. There is no obvious porosity in planar or cross-polarised light. Using fluorescence microscopy, overall structure of the pore system, consisting out of very fine connections between small pores can be visualised. However, the analysis of these images would lead to an overestimation of the total porosity, due to the very bright fluorescence of the resin.

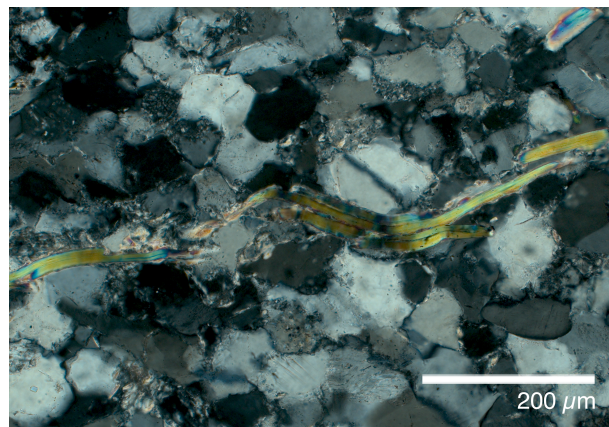


Figure 1.23: Photomicrograph (XPL) of Kandla Grey. The bright, elongated minerals are micas. Further the stone is dominated by quartz and (weathered) feldspars.

Using BSE images, the morphology of the solid phase and pores can be examined. In figure 1.24 mica minerals between the quartz grains can be seen. It is obvious that the structure of Kandla Grey is very dense and the stone has a quartzite-like appearance. EDS analysis (figure 1.25) was used to identify the different minerals. Again, red indicates iron, green represents potassium and indicates the presence of feldspars, blueish green represents mica minerals containing both potassium and aluminium. The

yellow grain originates from the EDS signal of titanium, meaning the dense minerals that are also observed using optical microscopy are presumably rutile.

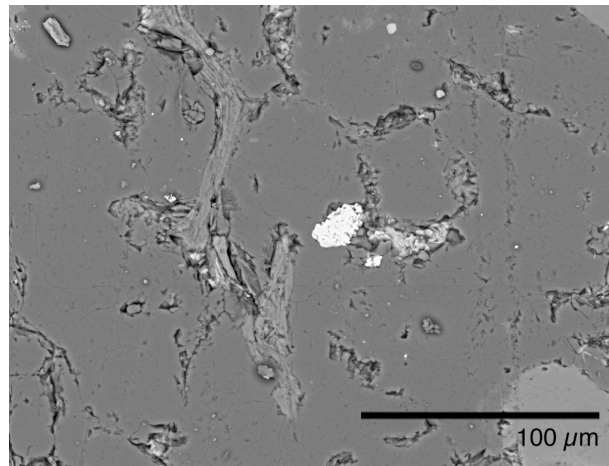


Figure 1.24: BSE image of Kandla Grey, showing micas between the main quartz material.

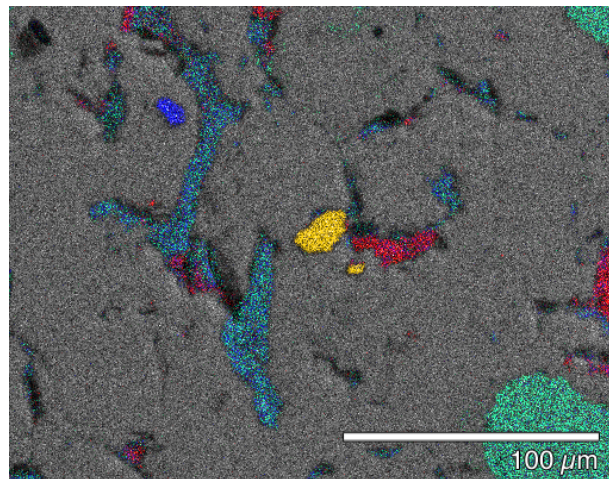


Figure 1.25: EDS maps for silicon (grey), potassium (green), aluminium (blue), iron (red) and titanium (yellow). Measurements were performed on the same area as figure 1.24.

Characterisation tests

Kandla Grey is a very compact sandstone, with a measured open porosity of around 3 vol.% and an apparent density of over 2600 kg/m³. (table 1.1). The material has a low capillary absorption coefficient of 2.96 g.m⁻².s^{-1/2}. During tests, it was shown that mica-rich laminations inside the sandstone were preferential flow paths for water (Cnudde et al., 2013). Powder X-ray diffraction patterns revealed that these micas consist out of muscovite and chlorite.

References

- A. Ammouche, J. Riss, D. Breysse, and J. Marchand. Image analysis for the automated study of microcracks in concrete. *Cement and Concrete Composites*, 23(2-3):267–278, apr 2001. ISSN 09589465. doi: 10.1016/S0958-9465(00)00054-8.
- G. F. Andriani and N. Walsh. Physical properties and textural parameters of calcarenitic rocks: qualitative and quantitative evaluations. *Engineering Geology*, 67(1-2):5–15, dec 2002. ISSN 00137952. doi: 10.1016/S0013-7952(02)00106-0.
- F. S. Anselmetti, S. Luthi, and G.P. Eberli. Quantitative Characterization of Carbonate Pore Systems by Digital Image Analysis. *AAPG Bulletin*, 82(10):1815–1836, 1998.
- P. Bésuelle, J. Desrues, and S. Raynaud. Experimental characterisation of the localisation phenomenon inside a Vosges sandstone in a triaxial cell. *International Journal of Rock Mechanics and Mining Sciences*, 37(8):1223–1237, dec 2000. ISSN 13651609. doi: 10.1016/S1365-1609(00)00057-5.
- J. Bisschop and J.G.M. van Mier. How to study drying shrinkage microcracking in cement-based materials using optical and scanning electron microscopy? *Cement and Concrete Research*, 32(2):279–287, feb 2002. ISSN 00088846. doi: 10.1016/S0008-8846(01)00671-8.
- S. Bourquin and M. Durand. International Field Workshop on The Triassic of eastern France , 2006. URL <https://geosciences.univ-rennes1.fr/IMG/pdf/EasternTriassicFrance.pdf>.
- E-M. Charalampidou, S. A. Hall, S. Stanchits, H. Lewis, and G. Viggiani. Characterization of shear and compaction bands in a porous sandstone

- deformed under triaxial compression. *Tectonophysics*, 503(1-2):8–17, apr 2011. ISSN 00401951. doi: 10.1016/j.tecto.2010.09.032.
- V. Cnudde, J. Dewanckele, W. De Boever, L. Brabant, and T. De Kock. 3D characterization of grain size distributions in sandstone by means of X-ray computed tomography. In *Quantitative mineralogy and microanalysis of sediments and sedimentary rocks*, pages 99–113. 2012.
- V. Cnudde, W. De Boever, J. Dewanckele, T. De Kock, M. Boone, M.N. Boone, G Silversmit, L. Vincze, E Van Ranst, H Derluyn, S Peetermans, J Hovind, P Modregger, M Stamparoni, K De Buysser, and G De Schutter. Multi-disciplinary characterization and monitoring of sandstone (Kandla Grey) under different external conditions. *Quarterly Journal of engineering Geology and Hydrogeology*, 46:95–106, 2013. doi: 10.1144/qjegh2012-005.
- E. Colas, J. D. Mertz, C. Thomachot-Schneider, V. Barbin, and F. Rassineux. Influence of the clay coating properties on the dilation behavior of sandstones. *Applied Clay Science*, 52(3):245–252, 2011. ISSN 01691317. doi: 10.1016/j.clay.2011.02.026.
- C. W. Dubelaar and T. G. Nijland. Early Cretaceous Obernkirchen and Bentheim Sandstones from Germany used as dimension stone in the Netherlands: geology, physical properties, architectural use and comparative weathering. *Geological Society, London, Special Publications*, mar 2015a. ISSN 0305-8719. doi: 10.1144/SP416.13.
- C. W. Dubelaar and T. G. Nijland. The Bentheim Sandstone: Geology, Petrophysics, Varieties and Its Use as Dimension Stone. *Engineering Geology for Society and Territory*, 8:557–563, 2015b. doi: 10.1007/978-3-319-09408-3.
- M. Duser, R. Dreesen, and A. De Naeyer. *Renovatie & Restauratie - Natuursteen in Vlaanderen, versteend verleden*. Kluwer, 2009.
- J-C. Gall and L. Grauvogel-Stamm. The early Middle Triassic Grès à Voltzia Formation of eastern France: a model of environmental refugium. *Comptes Rendus Palevol*, 4(6-7):637–652, sep 2005. ISSN 16310683. doi: 10.1016/j.crpv.2005.04.007.
- Hans Chr Gran. FLUORESCENT LIQUID REPLACEMENT TECHNIQUE . A MEANS OF CRACK DETECTION AND

WATERBINDER RATIO DETERMINATION IN HIGH STRENGTH CONCRETES. 25(5):1063–1074, 1995.

- M. G. Gustafsson. Surpassing the lateral resolution limit by a factor of two using structured illumination microscopy. *Journal of microscopy*, 198(Pt 2):82–7, may 2000. ISSN 0022-2720.
- R. Heintzmann and G. Ficz. Breaking the resolution limit in light microscopy. *Briefings in functional genomics & proteomics*, 5(4):289–301, dec 2006. ISSN 1473-9550. doi: 10.1093/bfpg/ell036.
- S. Hillier. Pore-lining chlorites in siliciclastic reservoir sandstones, electron microprobe, SEM and XRD data and implication for their origin. *Clay Minerals*, 29:665–679, 1994.
- K.O. Hoal, J.G. Stammer, S.K. Appleby, J. Botha, J.K. Ross, and P.W. Botha. Research in quantitative mineralogy: Examples from diverse applications. *Minerals Engineering*, 22(4):402–408, mar 2009. ISSN 08926875. doi: 10.1016/j.mineng.2008.11.003.
- Z. Huang, J. Chen, H. Xue, Y. Wang, M. Wang, and C. Deng. Microstructural characteristics of the Cretaceous Qingshankou Formation shale, Songliao Basin. *Petroleum Exploration and Development*, 40(1):61–68, feb 2013. ISSN 18763804. doi: 10.1016/S1876-3804(13)60006-3.
- J. Ingham. *Geomaterials under the microscope*. Academic Press, 2013. ISBN 978-0-12-407230-5.
- S. Jacobsen, H. C. Granl, E. J. Sellevold, and J. A. Bakke. High Strength Concrete - Freeze/Thaw Testing and Cracking. *Cement and Concrete Research*, 25(8):1775–1780, 1995.
- K. Jiao, S. Yao, C. Liu, Y. Gao, H. Wu, M. Li, and Z. Tang. The characterization and quantitative analysis of nanopores in unconventional gas reservoirs utilizing FESEMFIB and image processing: An example from the lower Silurian Longmaxi Shale, upper Yangtze region, China. *International Journal of Coal Geology*, 128-129: 1–11, aug 2014. ISSN 01665162. doi: 10.1016/j.coal.2014.03.004.
- T.J. Katsube and M.A. Williamson. EFFECTS OF DIAGENESIS ON SHALE NANO-PORE FOR SEALING. *Clay Minerals*, 29:451–461, 1994.

- W. D. Keller. Kaolinization of feldspar as displayed in scanning electron micrographs. *Geology*, 6(march):184–188, 1978. doi: 10.1130/0091-7613(1978)6<184.
- E Klein and T Reuschle. A model for the mechanical behaviour of Bentheim sandstone in the brittle regime. *Pure and Applied Geophysics*, 160(5-6):833–849, 2003. doi: 10.1007/pl00012568.
- C. E. Krohn and H Thompson. Fractal sandstone pores: automated measurements using scanning-electron-microscope images. *Physical Review B*, 33(9):6366–6374, 1986.
- S. D. Leith, M. M. Reddy, W. F. Ramirez, and M. J. Heymans. Limestone Characterization to Model Damage from Acidic Precipitation: Effect of Pore Structure on Mass Transfer. *Environmental Science & Technology*, 30(7):2202–2210, 1996.
- G. E. Lloyd. Atomic Number and Crystallographic Contrast Images with the SEM: A Review of Backscattered Electron Techniques. *Mineralogical Magazine*, 51(359):3–19, 1987. ISSN 0026-461X. doi: 10.1180/minmag.1987.051.359.02.
- M. W. Longman and P. A. Mench. Diagenesis of cretaceous limestones in the edwards aquifer system of south-central texas: a scanning electron microscope study. *Sedimentary Geology*, 21:241–276, 1978.
- K. Malaga-Starzec, U. Åkesson, J.E. Lindqvist, and B. Schouenborg. Microscopic and macroscopic characterization of the porosity of marble as a function of temperature and impregnation. *Construction and Building Materials*, 20(10):939–947, dec 2006. ISSN 09500618. doi: 10.1016/j.conbuildmat.2005.06.016.
- S. Margolis and R. W. Rex. Endolithic Algae and Micrite Envelope Formation in Bahamian Oolites as Revealed by Scanning Electron Microscopy. *Geological Society of America Bulletin*, 82(April):843–852, 1971. doi: 10.1130/0016-7606(1971)82.
- J. Matějčíček, B. Kolman, J. Dubský, K. Neufuss, N. Hopkins, and J. Zwick. Alternative methods for determination of composition and porosity in abradable materials. *Materials Characterization*, 57(1):17–29, jul 2006. ISSN 10445803. doi: 10.1016/j.matchar.2005.12.004.
- A. Neville. How closely can we determine the water-cement ratio of hardened concrete? *Materials and Structures*, 36(June):311–318, 2003.

- T. G. Nijland, C. W. Dubelaar, R. P. J. van Hees, and T. J. M. van der Linden. Black weathering of Bentheim and Obernkirchen sandstone. *Heron*, 48 (3):179–195, 2003a.
- T. G. Nijland, W. Dubelaar, R. Van Hees, and T. Van Der Linden. De Bentheimer zandsteen : oliereservoirsteente en bouwsteen. *Grondboor & Hamer*, 57(2):21–25, 2003b.
- T. Nishiyama and H. Kusuda. Identification of pore spaces and microcracks using fluorescent resins. *International Journal of Rock Mechanics and Mining Sciences & Geomechanics Abstracts*, 31(4):369–375, aug 1994. ISSN 01489062. doi: 10.1016/0148-9062(94)90904-0.
- I. O. Ojala. The effect of CO₂ on the mechanical properties of reservoir and cap rock. In J Gale, C Hendriks, and W Turkenberg, editors, *10th International Conference on Greenhouse Gas Control Technologies*, volume 4, pages 5392–5397. Elsevier Science Bv, Amsterdam, 2011. ISBN 1876-6102. doi: 10.1016/j.egypro.2011.02.523.
- O. A. Olafuyi, A. P. Sheppard, C. H. Arns, R. M. Sok, Y. Cinar, M. A. Knackstedt, and W. V. Pinczewski. Experimental Verification of Effect of Size on Drainage Capillary Pressure Computed from Digitized Tomographic Images. *International Journal of Engineering Research in Africa*, 1:1–10, 2010. doi: 10.4028/www.scientific.net/JERA.1.1.
- F. J. Pettijohn, P. E. Potter, and R. Siever. *Sand and Sandstone*. Springer US, New York, NY, 1973. ISBN 978-0-387-90071-1. doi: 10.1007/978-1-4615-9974-6.
- L. D. Poulikakos and M. N. Partl. Investigation of porous asphalt microstructure using optical and electron microscopy. *Journal of microscopy*, 240(2):145–54, nov 2010. ISSN 1365-2818. doi: 10.1111/j.1365-2818.2010.03388.x.
- T. Ramstad, N. Idowu, C. Nardi, and P. E. Oren. Relative Permeability Calculations from Two-Phase Flow Simulations Directly on Digital Images of Porous Rocks. *Transport in Porous Media*, 94(2):487–504, 2012. doi: 10.1007/s11242-011-9877-8.
- J. S. Ray. Age of the Vindhyan Supergroup: A review of recent findings. *Journal of Earth System Science*, 115(1):149–160, 2006. ISSN 02534126. doi: 10.1007/BF02703031.
- S.J.B. Reed. *Electron Microprobe Analysis and Scanning Electron*

- Microscopy in Geology*. Cambridge University Press, 2005. ISBN 9780521848756. doi: <http://dx.doi.org/10.1017/CBO9780511610561>.
- E. H. Rego, L. Shao, J. J. Macklin, L. Winoto, G. A. Johansson, N. Kamps-Hughes, M. W. Davidson, and M. G. L. Gustafsson. Nonlinear structured-illumination microscopy with a photoswitchable protein reveals cellular structures at 50-nm resolution. *Proceedings of the National Academy of Sciences of the United States of America*, 109(3): E135–43, jan 2012. ISSN 1091-6490. doi: 10.1073/pnas.1107547108.
- T. Rivas, B. Prieto, B. Silva, and J. M. Birginie. Weathering of granitic rocks by chlorides: effect of the nature of the solution on weathering morphology. *Earth Surface Processes and Landforms*, 28(4):425–436, apr 2003. ISSN 0197-9337. doi: 10.1002/esp.492.
- L. Schmitt, T. Forsans, and F.J. Santarelli. Shale Testing and Capillary Phenomena. *International Journal of Rock Mechanics and Mining Sciences*, 31(5):411–427, 1994.
- W. A. Shear, P. A. Selden, and J-C. Gall. Millipedes from the Grès à Voltzia, Triassic of France, with comments on Mesozoic millipedes (Diplopoda: Helminthomorpha: Eugnatha). *International Journal of Myriapodology*, 2(1):1–13, jun 2009. ISSN 18752535. doi: 10.1163/187525409X462395.
- P. Soroushian, M. Elzafraney, and A. Nossoni. Specimen preparation and image processing and analysis techniques for automated quantification of concrete microcracks and voids. *Cement and Concrete Research*, 33(12): 1949–1962, dec 2003. ISSN 00088846. doi: 10.1016/S0008-8846(03)00219-9.
- L. M. O. Sousa, L. M. Suárez del Río, L. Calleja, V. G. Ruiz de Argandoña, and A. R. Rey. Influence of microfractures and porosity on the physico-mechanical properties and weathering of ornamental granites. *Engineering Geology*, 77(1-2):153–168, feb 2005. ISSN 00137952. doi: 10.1016/j.enggeo.2004.10.001.
- A. Stadler. *Der Bentheimer Sandstein (Valangin, NW-Deutschland): Eine paleoökologische und sequenzstratigraphische Analyse*. PhD thesis, Ruhr-University Bochum, 1998.
- D. Sutherland. Estimation of mineral grain size using automated

- mineralogy. *Minerals Engineering*, 20(5):452–460, apr 2007. ISSN 08926875. doi: 10.1016/j.mineng.2006.12.011.
- C. Thomachot and D. Jeannette. Effects of iron black varnish on petrophysical properties of building sandstone. *Environmental Geology*, 47(1):119–131, 2004.
- A. Timur, W.B. Hemphkins, and R.M. Weinbrandt. Scanning electron microscope study of pore systems in rocks,. *Journal of Geophysical Research*, 76(20):4932–4984, 1971. doi: 10.1029/JB07i020p04932.
- K. E. Van Den Abeele, J. Carmeliet, P. A. Johnson, and B. Zinszner. Influence of water saturation on the nonlinear elastic mesoscopic response in Earth materials and the implications to the mechanism of nonlinearity. *Journal of Geophysical Research*, 107:1–11, 2002.
- T. Wajima, S. Okura, Y. Chen, M. Bessho, and T. Nishiyama. Observation of Pore Spaces and Microcracks Using a Fluorescent Technique in Some Reservoir Rocks of Oil, Gas and Geothermal Fields in the Green Tuff Region, Japan. *Resource Geology*, 50(3):191–200, sep 2000. ISSN 13441698. doi: 10.1111/j.1751-3928.2000.tb00069.x.
- L. Zhang, G. Bai, X. Luo, X. Ma, M. Chen, M. Wu, and Wenxiu Yang. Diagenetic history of tight sandstones and gas entrapment in the Yulin Gas Field in the central area of the Ordos Basin, China. *Marine and Petroleum Geology*, 26(6):974–989, jun 2009. ISSN 02648172. doi: 10.1016/j.marpetgeo.2008.05.003.

2

X-ray micro-computed tomography (μ CT)

This chapter will describe the basic principles of X-ray computed tomography, the main analysis technique used in this work. Both history and current developments of the method will be covered, as well as the setups that were used in this thesis. Further, a brief introduction on data manipulation and analysis will be provided.

2.1 Introduction

X-ray computed tomography is an imaging technique that uses X-rays as penetrating probe. These X-rays are electromagnetic radiation with a wavelength between 0.01 and 10 nm. X-rays have a large penetration ability inside matter, and are therefore used to look inside or through objects, e.g. in medical applications or (airport) security. X-rays were discovered by W. Röntgen in 1895 and were very fast applied for medical applications, where they still are one of the most used techniques for diagnostics. Although radiographs, which are 2D projections of a 3D object after X-ray penetration, provide valuable information, they lack depth information, which can lead to misinterpretation of the images. As a solution, computerised axial tomography scanning (CAT or CT) was developed by Hounsfield (Hounsfield, 1973). CT combines information from many radiographs, taken at numerous angles around an object, and transforms them into a 3D representation of the internal structure of the object. Although the method was designed for medical purposes, its unique ability to look inside non-transparent objects without destroying them, enabled it to be quickly adopted in many other scientific fields. A major disadvantage of the use of medical CT scanners is that they are designed to scan patients, and the spatial resolution is limited to several hundreds of micrometres. This resolution problem initiated the development of a new research field: High resolution X-ray tomography (HRXCT) or X-ray micro-computed tomography (μ CT). The method evolved rapidly over the past two decades, with vast improvements in both temporal and spatial resolution. The resolution of these systems is typically between 1 and 50 μ m, but higher resolutions (down to several tens of nm) are possible, both in laboratory systems and at synchrotron facilities.

2.2 X-ray micro-computed tomography

2.2.1 Basic principles

X-ray computed tomography provides 3D structural information of materials at (sub-)micron to millimetre scale. This makes the technique exceptionally suited for multi-scale characterisation of these materials. The method is based on the attenuation of X-rays when they travel through

material, expressed by the Lambert-Beer law. This law is presented in equation 2.1 and describes how X-rays are attenuated when they travel through a homogeneous material; transmitted X-ray intensity I depends on the incident intensity I_0 and the linear attenuation coefficient $\mu(s)$ along the raypath s .

$$I = I_0 e^{-\int \mu(s) ds} \quad (2.1)$$

The Lambert-Beer law is only valid for a monochromatic X-ray beam, and lab-based X-ray CT systems are equipped with an X-ray source that produces polychromatic X-rays. This influences the measurement of the attenuation coefficient and causes imaging artefacts, which will be described later in this work. Since the linear attenuation coefficient μ depends on the atomic number of the elements in the sample, the density of the sample and the beam energy, direct elemental information is not easily obtained using X-ray CT. X-rays can interact with the material in the sample in different ways, and a combination of these interactions will determine the attenuation coefficient of a material. For μ CT, the most relevant interactions are *photoelectric absorption*, *Compton scattering* and *Rayleigh scattering* (figure 2.1).

Photoelectric absorption occurs when an X-ray photon transfers its energy to an electron of an atom it hits. When this energy exceeds the binding energy of the electron, this electron is ejected from its atomic shell and emitted as a *photoelectron*. The photon energy is completely absorbed by the electron and the difference in binding energy of the electron and the X-ray photon energy is the kinetic energy of the photoelectron. With increasing photon energy, electrons from lower electron shells (closer to the atom core) can be ejected. This causes so-called *absorption edges*, related to the binding energies of different electron shells, hence they are named after their corresponding shells. As these binding energies are element specific, absorption edges are related to the atomic number of the elements the X-rays interact with. When an electron is liberated from an atom, an electron from a higher electron shell will fill in the gap that is created. In this process, the 'jumping' atom comes in a lower energy state and will emit its energy surplus in the form of a fluorescent X-ray photon, known as the *characteristic X-rays* of an element. These characteristic X-rays can be analysed by X-ray fluorescence spectroscopy (XRF) to determine the elemental composition of an unknown material, but cannot be used for absorption tomography purposes.

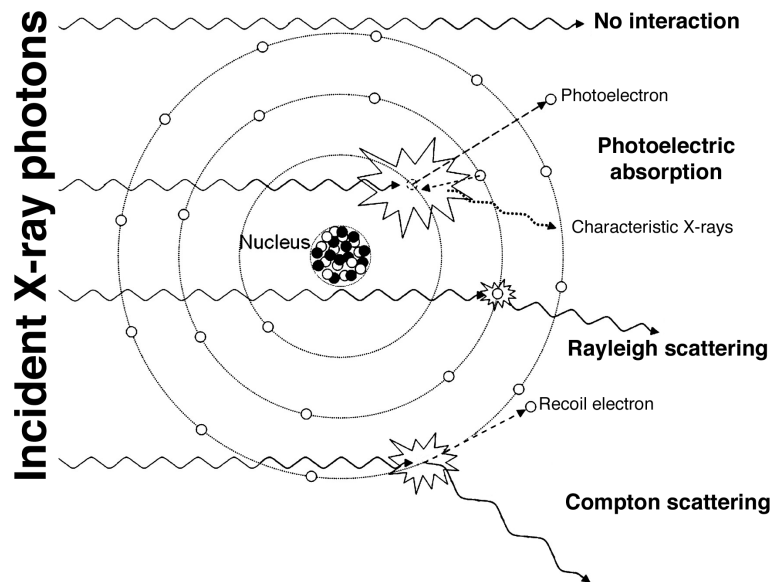


Figure 2.1: Different interactions of X-rays with matter, adapted from (Seibert and Boone, 2005).

Compton scattering occurs when the energy of the X-ray photon is a lot higher than the binding energy of the interacting electron, so that the photon cannot transfer all its energy to the electron. The photon will be deviated (*scattered*) by the electron and the electron will be ejected with an energy equal to the energy loss of the X-ray photon. Since Compton scattering depends very little on the type of material, it is of much higher relative importance for low atomic number elements, where contribution of the photoelectric effect is low. Since the X-rays are deviated but not stopped, they can still be detected by the X-ray detector. If this detector is placed sufficiently far, contribution to the detected X-rays by Compton scattering will be constant and will not hinder image quality. However, when the detector position is close to the sample, Compton scattering will cause artefacts that are hard to correct for (Boone, 2014; Vlassenbroeck, 2009).

Rayleigh scattering is scattering of X-ray photons on the entire electron cloud, rather than individual electrons. The photon loses almost no energy

but the deviation from its initial trajectory can be very big. In general, however, the effect of Rayleigh scattering in X-ray imaging is negligible.

The linear attenuation coefficient (μ) is the combined result of the three interactions described above, and therefore strongly depends on the atomic number Z of the sample's material and the energy of the X-ray photons (E). μ can be approximated as the sum of Compton scattering and photoelectric absorption.

$$\mu = \rho_e(\sigma_c + \frac{bZ^3}{E^3}) \quad (2.2)$$

In this equation, ρ_e is the electron density, b is a constant and σ_c is the Compton active cross-section per electron.

$$\rho_e = \rho \frac{Z}{A} N_A \quad (2.3)$$

Electron density depends on the density of the material (ρ), the atomic number Z , the atomic weight A and Avogadro's number N_A . Photoelectric absorption is the dominant interaction for low X-ray energies, especially for lower values of Z , thus in for low energy X-rays, attenuation will be dominated by the elemental composition of samples. At higher energies, Compton scattering will be dominant and electron density will be the determining factor for X-ray attenuation (Boone, 2015).

2.2.2 μ CT setup

An X-ray CT setup consists of an X-ray source and detector, which rotate around the sample in medical CT setups, but are generally fixed with a rotating sample in CT setups designed for materials science (figure 2.2). The sample is positioned between the source and detector, resulting in a radiograph recorded at the detector. Sample thickness, composition and density determine the intensity of the X-rays reaching the detector. Over an angular range of 360 (or 180) degrees, several hundreds to thousands of radiographs are recorded, and using reconstruction algorithms (Vlassenbroeck et al., 2007), these data are transformed into a 3D volume. This volume is a 3D distribution of the linear attenuation coefficient, represented by a specific grey value, often stored as a stack of virtual 2D slices. When computed tomography is used for imaging samples at high (1

to 50 μm) resolutions, it is called micro-tomography (μCT). Two main types of μCT systems exist, lab-based systems (figure 2.2) and synchrotron systems (figure 2.3). In synchrotron setups, X-rays are generated by the rapid acceleration of electrons in a large 'storage ring'. The size of this storage ring causes the production of a parallel X-ray beam, which rules out so-called cone-beam artefacts present in lab-based images (see section 2.8). The beam has a much higher brilliance than the radiation produced by laboratory X-ray tubes. Although this beam is also polychromatic, it is possible to send it through a monochromator and still preserve enough of the X-ray flux for tomography. X-ray intensity is converted into light by a scintillator screen, and magnification is obtained by optics. The high brilliance at synchrotron beam lines results in a clear superiority in terms of achievable spatial resolution and signal-to-noise ratio (Baruchel et al., 2006), but the number of synchrotron facilities is limited and the operational cost is very high. In lab-based systems, X-rays are generated by an X-ray tube in which electrons are produced by a filament (cathode) and accelerated towards a target (anode), often composed of tungsten or molybdenum. These electrons hit the target at high speeds, and through rapid deceleration, their energy is converted into heat and X-ray radiation, known as *Bremsstrahlung*. This radiation is polychromatic, and depends on the target material and the accelerating voltage of the electrons. Although these systems (Jakubek et al., 2006; Masschaele et al., 2007) have lower X-ray flux, they are more cost-efficient. Nowadays, a large number of desktop CT systems are commercially available, making micro-CT accessible for a large number of researchers. Lab-based setups come in all sizes, making investigation of geomaterials possible using sample sizes ranging from the core scale (where often medical CT scanners are still used) up to very small microplugs ($<1\text{ mm}$). Even large-scale objects such as freight containers (Firsching et al., 2013) and tree logs up to 1 m in diameter (Alkan et al., 2007; Longuetaud et al., 2004) can be imaged using adapted setups.

2.2.3 Resolution

In laboratory X-ray CT setups, high-resolution imaging is typically achieved by geometrical magnification of a sample, using a cone-shaped X-ray beam (figure 2.2). The resolution of these setups is mainly limited by the focal spot size of the X-ray tube, under the condition that the voxels are smaller than this spot size (Cnudde et al., 2006; Ketcham and Carlson,

2001). Therefore, in order to reach high resolutions, this focal spot size needs to be as small as possible. To create a small focal spot, the electrons are electrostatically and magnetically focused on the target (Boone, 2014). In high-end, commercially available X-ray tubes, the smallest spot size is about 400 nm (Van Loo et al., 2013), although recent work has led to the development of tubes with spot sizes down to 100 nm (Espes et al., 2015). In most cases, the reconstructed voxel size is larger than the spot size, however, and the terms voxel size and spatial resolution are often used as synonyms in μ CT. In order to achieve maximum magnification, samples need to be positioned very close to the X-ray source, and therefore resolution is also influenced by the sample size. The ratio between the source-object distance (SOD) and source-detector distance (SDD) controls the magnification, and together with spot size s and the detector pixel size d , this determines the resolution R , or the effective voxel size (Equation 2.4). The maximum effective voxel size depends on the configuration of a specific setup.

$$R = \frac{d}{M} + (1 - \frac{1}{M})s \quad M = \frac{SDD}{SOD} \quad (2.4)$$

In the rest of this work, all references to μ CT are linked to lab-based CT, unless it is clearly stated differently in the text.

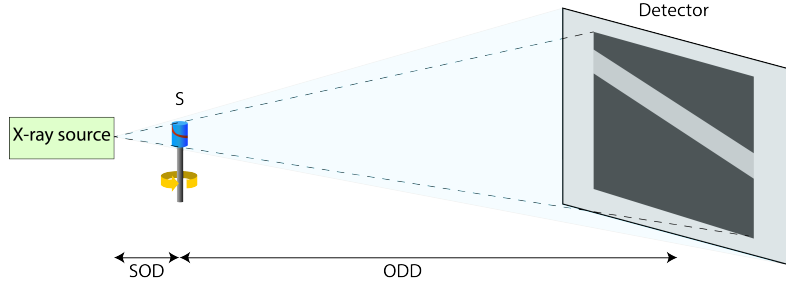


Figure 2.2: Schematic representation of a typical laboratory μ CT setup, equipped with an X-ray tube and using a cone-beam configuration. A sample (S) is positioned between the source and the X-ray detector.

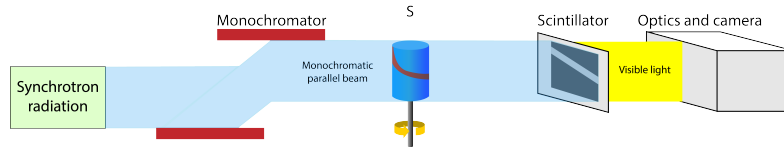


Figure 2.3: Schematic representation of a typical synchrotron μ CT setup

Partial volume effect

μ CT images (and other types of images) are rasterised representations of reality. This means that all features that are smaller than the voxel or pixel size will never be identified as separate objects. However, every feature that fits completely or partially inside a pixel or voxel will contribute proportionally to the colour or grey value of that raster element, a phenomenon called the *partial volume effect*. Due to the partial volume effect, features that are essentially one pixel or voxel wide will usually be smeared over multiple voxels, since the chance that this element is precisely aligned with the image grid is close to zero. This means that the partial volume effect will be less important where large objects are imaged at high resolution. The closer an object's size is to the actual voxel size, the harder it will be to identify it as an object.

The partial volume effect is demonstrated by figure 2.4. A and B show the same objects, three grains of different size and represented by a different grey value, with a crack through the upper right object. In A, this object is imaged with a relatively large pixel size, in example B the pixel size is 5 times smaller. C and D are the respective resulting images of both examples. In figure 2.4 C, the main disadvantage of the effect is obvious: the image is very blurry since there is not enough difference between the object size and the pixel size. The crack and small upper left object are completely lost, but you can still clearly see that there are two larger objects. However, little information is provided about the size and shape of these objects. In figure 2.4 D, the edges are much sharper and the two largest objects can be identified as circles. The upper left object can be seen, albeit unsharp. The crack in the upper right object in B can be observed due to the partial volume effect, explaining the advantage of this effect. Even if objects fall below the resolution of an image, they can still be observed and in some cases information is provided about the orientation of sub-resolution objects.

In homogeneous samples that consist entirely of the same material, the

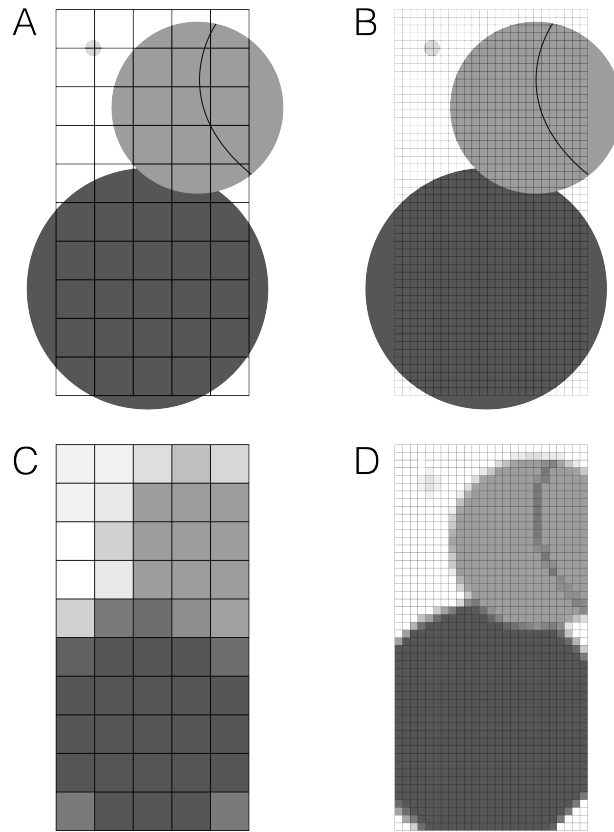


Figure 2.4: Demonstration of the partial volume effect. A: three objects imaged with a large pixel size. B: same objects imaged with a 5 times smaller pixel size. C: result of A. D: result of B.

variation in grey value caused by the partial volume effect can enable users to estimate the degree of microporosity, on the condition that there are also areas with 100 % porosity and entirely solid areas in the image. This can be compared to the estimation of microporosity using fluorescence light microscopy.

2.3 μ CT: Data acquisition and analysis

2.3.1 Image reconstruction

In order to go from a series of projections or radiographies to a 3D volume, so called tomographic reconstruction algorithms are used. In traditional μ CT, the projections are converted into attenuation images, and filtered backprojection is used to go from 2D attenuation images to a 3D representation of an object. Note that in the explanation below, a parallel beam is used to make everything more clear, whereas a cone beam is used in most laboratory μ CT setups. In figure 2.5 A, three attenuation images

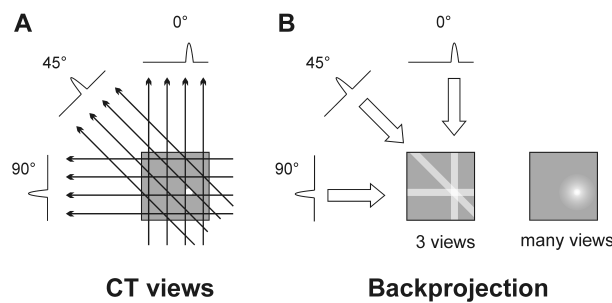


Figure 2.5: A: Representation of 3 projections through an object (white dot) using a parallel X-ray beam. B: Backprojection of this object using 3 attenuation images or an infinite amount of attenuation images. From Boone (2015).

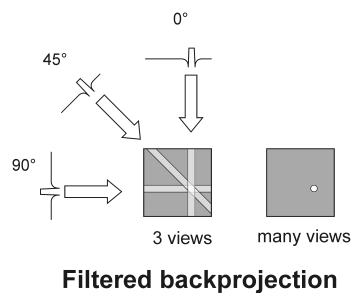


Figure 2.6: Representation of the principle of filtered backprojection. From Boone (2015).

of an object, in this case the white dot, are represented. The X-rays that interact with the volume are attenuated, while the others reach the detector

without interaction. To acquire information about the white dot, the attenuation images have to be backprojected along the X-ray path. While this is only shown for 3 attenuation images in the figure, this is done for many projections in real experiments (figure 2.5 B). Each projection is smeared out in its original direction, and this way, the original object can be reconstructed. As can be seen in figure 2.5 B, there is heavy blurring around the edges, making this image not useable for analysis of the original object. Therefore, a filter is applied on the projections, and so-called *filtered backprojection* is performed on these filtered images. The filter flattens the top of the pulse, so that the entire dot has the same attenuation and negative spikes at the side of the pulse counteract the blurring. After the backprojection, a correct reconstruction of the object is acquired (figure 2.6).

2.3.2 Image processing

Before adequate analysis of images can be performed, it is paramount to ensure the quality of the images is sufficient. Therefore, the correct acquisition parameters should be selected to obtain the best image possible. However, even with the highest care during acquisition, X-ray tomography is still prone to noise. Signal-to-noise ratio can be improved by increasing the number of photons hitting the detector, thus increasing the number of projections, using a higher exposure time or the acquisition of multiple frames at one angular interval. All of these measures cause higher scan times, which might be unwanted for samples prone to radiation damage or when high scan speeds are needed to visualise dynamic processes (Bultreys et al., 2015). Noise can also be reduced after image acquisition and this is called *image processing*. This step usually consists of adjusting contrast and brightness, grey scale range and filtering the images.

2.3.3 Image analysis

For quantitative analysis of 2D images and 3D datasets, data should be analysed using dedicated software. For 2D image analysis, there is a huge amount of software available, ranging from very good open source tools to well-known commercial packages such as Adobe Photoshop. Although the market for 3D analysis software is much younger, more and more

excellent tools are becoming available. At the moment, some of the best software packages include Avizo (www.avizo.com), VGStudioMAX (www.volumegraphics.com), MAVI (www.itwm.franhofer.de), Pore3D (Brun et al., 2010), 3DMA-Rock (Lindquist and Venkatarangan, 1999), Morpho+ (also known as Octopus Analysis, distributed by www.insidematters.eu; Brabant et al. (2011); Vlassenbroeck et al. (2007)) and Fiji (open source, www.fiji.sc; Schindelin et al. (2012)). Quantitative results from this 3D analysis include data on the overall structure and texture of a material, component volume fractions, pore and grain size and morphology parameters (shape, sphericity, roundness, etc.), and many more (Cnudde et al., 2012). In practice, quantitative 3D analysis is often not straightforward and can be prone to several systematic errors caused by e.g. image noise or discretization effects. Furthermore, many analyses require significant user input, so special attention has to be taken to the interpretation of results. It is essential that researchers are aware of the limitations and pitfalls whilst recording or analyzing data (Cnudde and Boone, 2013). In the following, some key image analysis methods described in the literature are discussed, with an emphasis on 3D analysis (although many of the measurements are directly applicable to 2D images as well). When analyses are performed directly on grey value images, image noise and sharpness can be an issue. Furthermore, small bright spots (resulting for example from highly attenuating minerals) can result in difficult measurements and interpretations (Wildenschild and Sheppard, 2013). Other measures demand the partition of voxels into material phases, instead of working on grey values. This requires that the provided image quality is high and that image artefacts related to the used technique are reduced as much as possible by selecting the correct hardware and software setup, the best acquisition and reconstruction parameters and possibly by performing image processing after the data acquisition (Bovik et al., 2001; Russ, 2002). Then, the next step in the analysis process is image segmentation. Image segmentation means that each voxel in the 3D region of interest is assigned a label according to the material it is assumed to belong to. Because segmentation is typically the first step in the processing, it plays a crucial role in errors and uncertainties related to pore characterisation from experimental methods. The easiest method to segment an image consists of using a single threshold: all values within a certain grayscale interval are assigned to a certain material phase. Although many automated methods for threshold selection are available (Huang and Wang, 1994; Ridler and Calvard, 1978; Otsu, 1979) this step

is very often performed manually, and is therefore user-dependent. Dual thresholding (often also referred to as hysteresis thresholding) uses two intervals; voxels with a grey value in the first interval are classified as a certain material phase, while voxels in the second interval are only considered to belong to this phase if they are connected to voxels from the first interval (Brabant et al., 2011). This approach reduces the sensitivity to residual image noise. Obviously, manual adjustment of thresholds to produce a result that is considered to be correct based on visual inspection by a human operator has to be reduced as much as possible. User-dependency is one of the major drawbacks of image-based analysis methods, since it implies that results on the same data can vary between different users and research institutions. Automated threshold methods are a vital part of the solution to this problem, but the diversity of applications, image types and image artefacts makes this a very challenging task. Another problem with the previously discussed thresholding techniques, is that every voxel in the image is treated the same, i.e. no local information is taken into account when deciding to which phase a certain voxel belongs. This poses problems when not all voxels of a certain material phase fall in the same grey value range, for example due to beam hardening (see section 2.8). Furthermore, the use of local information is a powerful way to reduce misclassification due to statistical noise. It can help to segment phases with low contrast by including edge information, and it often reduces user dependency (many of these methods ask user input to pin down the phase of voxels which are easy to segment, and then automatically segment the difficult parts of the image). Several of these segmentation methods exist, but a detailed description of all image segmentation methods would justify a review on its own. All segmentation methods (automatic methods in particular) make some assumptions about the nature of the image, and in order to choose the proper algorithm, it is important to know as much as possible about the nature of the image, how it was acquired, and what kinds of structure are present in it (Russ, 2002). A comprehensive survey of many techniques is available in Sezgin and Sankur (2004), while the review by Iassonov et al. (2009) compares advanced segmentation methods for X-ray micro-CT scans of porous materials in particular. As can be seen in these review articles, many automatic segmentation methods have been devised, but in practice segmentation typically still requires user intervention, resulting in subjectivity. Segmentation is often a bottle neck in the image analysis process, in particular for images with low contrast-to-noise ratio or which

contain certain artefacts. After segmentation, voxels that are erroneously classified as foreground voxels due to noise can sometimes be removed by applying several binary operations like eroding, dilating, opening, closing, and hole filling (Soille, 1999). However, when attention has been paid towards the production of high quality images with good contrast and an experienced user is controlling the 3D analysis software, excellent data can be obtained, giving valuable information about the materials structure. Once an experimental structural representation has been obtained and segmented, it is possible to assess geometrical properties of a pore space, individual grains or certain mineral phases (Brabant et al., 2011). The previously mentioned statistical measurements can be performed on segmented images and are then easier to interpret (Arns et al., 2005; Blair et al., 1996; Torquato, 2002; Wildenschild and Sheppard, 2013). The homogeneity of the medium can also be checked by measuring partial porosity, local porosity and local percolation. Other important measures are porosity, percolating porosity and (specific) pore surface area (possibly divided into pore surface in contact with certain minerals). By calculating the Euclidean distance map (in which every point is assigned a value representing its distance to another phase, every local maximum is a unique point that represents one specific feature) on the segmented image and performing a watershed transformation, the pore space can be divided into individual pores, separated at the pore throats, or the stone's matrix can be separated in individual grains (figure 2.7) (Brabant et al., 2011; Vincent and Soille, 1991). Once this separation has been performed, pore or grain shape can be quantified by determining individual pore volume, surface area, form factor (to characterise roughness) and the diameter of the largest inscribed and smallest circumscribed sphere. More advanced methods use ellipse fitting or spherical harmonics to describe 3D pore or grain shape (Wildenschild and Sheppard, 2013).

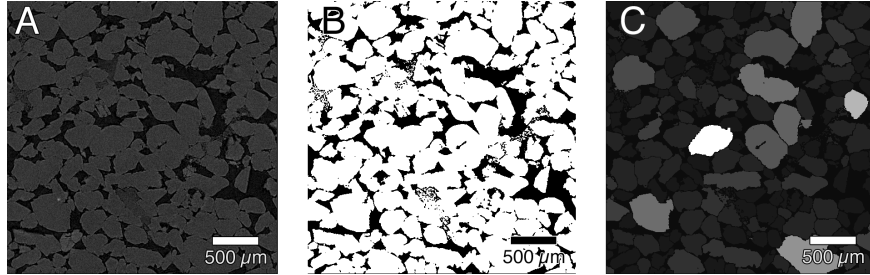


Figure 2.7: A: 2D slice of a reconstruction of a CT scan of Bentheim sandstone. B: Binary image where grains are white and pores black. C: Individual grains are separated and classified from small (dark) to large (bright).

2.3.4 Image artefacts

μ CT image acquisition gives rise to different types of image artefacts. These artefacts can be reduced by applying measures during acquisition, during reconstruction, or as an image processing step. Below some of the most common image artefacts in lab-based μ CT are discussed together with their origin and their possible solutions:

X-ray sources in lab-based CT typically produce a poly-chromatic X-ray beam. As the attenuation coefficient (equation 2.2) is energy-dependent, this gives rise to artefacts. Since low-energy photons are attenuated more than high-energy photons when the X-ray beam passes through the sample, the average energy of the X-ray beam reaching the detector increases, even though the overall intensity decreases, this phenomenon is called **beam hardening** (figure 2.8, A). Due to this effect, shorter ray paths through a sample (the edges of a sample) result in relatively higher measured attenuation coefficients than long ray paths (the centre of the sample) (Ketcham and Carlson, 2001). After reconstruction, this will appear as a brighter outside of the sample, even if the material is homogeneous. This is known as the cupping effect in the grey scale images. The beam hardening effect can be reduced by pre-hardening the beam by using a metal filter, or by correcting for it during reconstruction (Boone, 2014).

Ring artefacts (figure 2.8, B) occur because of locally faulty high or low intensities in projection images, usually because of defects in the detector. These ring artefacts can be reduced by taking a large number of flat-field images and by software corrections during reconstruction (Boone, 2014;

Ketcham and Carlson, 2001) .

Metal artefacts (figure 2.8, C) are present when very dense or heavy (mineral) phases are present in a sample. They are seen as dark streaks around these objects in cross sections. Only the photons with the highest energy are able to pass through the dense minerals, leading to very low attenuation and therefore dark streaks (Boone, 2014, 2015).

The geometry of lab-based systems with a cone-shaped X-ray beam leads to **cone beam artefacts** (figure 2.8, D). These take place since the analysed object is undersampled at the top and bottom of the images, which means that some parts of the top and bottom are not in the beam path at every projection angle. Therefore, horizontal features in these regions tend to be blurry or deformed and thus hard to analyse. Cone beam artefacts can be countered by using helical CT scanning, where the sample moves vertically during image acquisition.

Movement artefacts are caused by movement of the sample during the acquisition of the projections. They typically turn up as blurring in the reconstructed images. Possible causes are vibration of the setup unstable sample mounting or movement of the X-ray spot. Movement artefacts become more important at higher resolution, where more accuracy is needed. When imaging dynamic processes (Bultreys et al., 2015), movement artefacts are inevitable and can be reduced by 4D filtering algorithms.

2.4 The Centre for X-ray Tomography at Ghent University (UGCT)

The Centre for X-ray Tomography of Ghent University, the UGCT, was founded in 2006 by Prof. Dr. Luc Van Hoorebeke (Ghent University, Department of Physics and Astronomy) and Prof. Dr. Patric Jacobs (Ghent University, Department of Geology and Soil Science). The UGCT is an interdisciplinary centre performing research on the technique and applications of X-ray micro- and nanotomography. In its present form, the UGCT is an interfaculty collaboration between the Radiation Physics group (Dept. of Physics and Astronomy), the Laboratory for Wood Technology (WoodLab, Dept. of Forest and Water Management), led by prof. Joris Van Acker, and the PProGress group (Dept. of Geology and

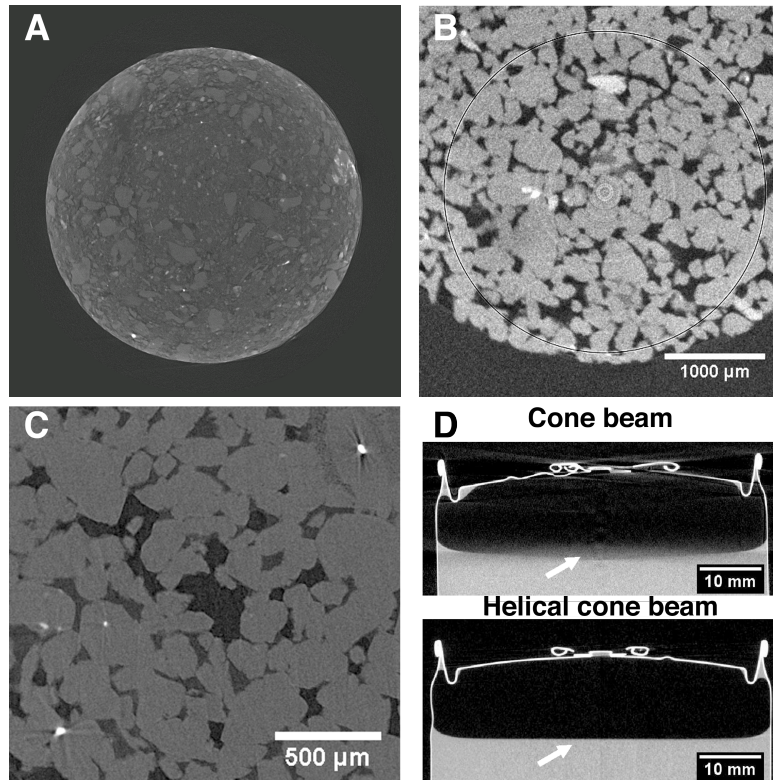


Figure 2.8: Examples of μ CT image artefacts. A: Beam hardening on a steel slag sample, from Boone (2015). B: Bentheim sandstone sample suffering from severe ring artefacts. C: Metal artefacts caused by heavy minerals in Bentheim sandstone. D: Top part of a soda can scanned in normal cone-beam geometry vs. helical scan to reduce cone-beam artefacts (from De Witte (2010)).

Soil Science) of Ghent University, led by prof. Veerle Cnudde. The centre has developed several modular μ CT setups, each capable of performing high-quality imaging on a large scale of sample sizes and kinds. Both hardware and software (for reconstruction and image analysis) are developed in-house, enabling control over every step in the analysis process.

2.4.1 Setups at the UGCT

In this section, the different setups at the UGCT are discussed. For each setup, the different hardware components are listed, special properties are mentioned, and the maximum spatial resolution is given. This spatial resolution was determined by taking radiographies and, in some cases, μ CT scans of line patterns representing a particular spatial resolution (<http://tinyurl.com/oxvsymf>).

Dual-head setup: 'The old scanner'

The first setup that was developed by the UGCT in 2005 is a dual-head system, created to be as flexible as possible, to allow imaging of all kinds of samples and providing the place for peripheral equipment (Masschaele et al., 2007). The old scanner used a FeinFocus system with two interchangeable X-ray heads as radiation source. The back part of the system, which took care of electron production, is fixed and is shared by both heads (figure 2.9). One of the heads was a directional head (FXE160.48), the other one was a transmission head (FXE160.51). The maximum accelerating voltage was 160 kV, and the main differences between both tube heads were the spot size that can be achieved and the X-ray flux they could produce.

In a directional tube, electrons hit the target, and X-rays are leave the target on the same side. Therefore, the target needs to be tilted, resulting in a larger and slightly asymmetrical X-ray spot. The advantage of this kind of tubes is that the back side of the target is free to add cooling, meaning more power can be applied, resulting in a higher X-ray flux. In a transmission tube, electrons hit the back of the target, and X-rays leave the target on the other side, being the front of the tube. As this does not allow the application of a cooling system, power and flux of these kind of tubes are limited. However, the spot size of this system was smaller, being around 700 nm at minimum (Cnudde et al., 2011).

The standard detector of the old scanner was a Varian PaxScan 2520V flat-panel detector, with a large surface area of 25 by 20 cm, corresponding to 1920 by 1536 pixels. The pixel size of this detector is 127 μ m. In the last few years, due to the development of other UGCT systems, the old scanner was mainly used for high-resolution experiments, since it could achieve spatial resolutions down to 0.9 μ m. The old scanner is currently decommissioned, and is being refurbished into MEDUSA. *Herakles* is the

newest UGCT scanner and is currently still under development. Herakles is a combination of a nano-focus X-ray tomography scanner, capable of performing CT at resolutions down to 500 nm and a micro-XRF system. After a full CT scan, it is possible to pinpoint areas of interest in the 3D volume and acquire the XRF spectrum at that precise location in order to obtain the chemistry of that exact point in space. The CT part of Herakles is equipped with an X-RAY WorX XWT-100 transmission tube with a maximum voltage of 100 kV and a focal spot of around 500 nm. The system has two interchangeable detectors: a PhotonicScience VHR with 1:1 optics and a Teledyne RadEye 1 small flat panel detector (1024 x 512 px; 48 m pixel size).

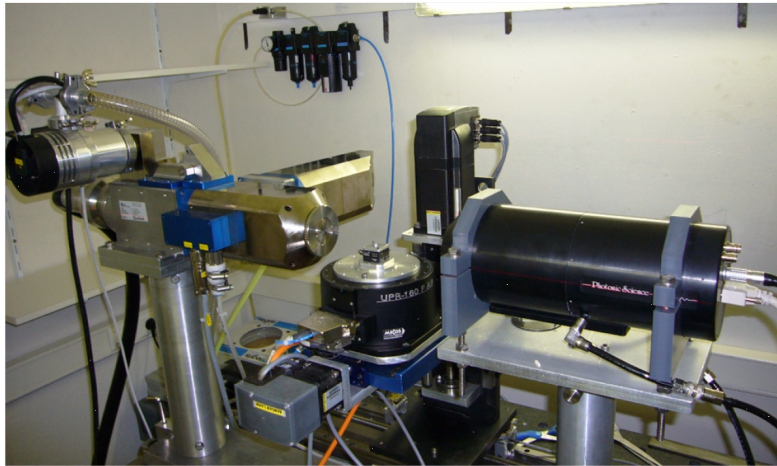


Figure 2.9: The 'old' scanner a.k.a. the dual-head setup.

MEDUSA

MEDUSA is one of the latest UGCT setups, and is currently still under development. Medusa can be seen as a refurbishment of the old scanner, reusing most of the parts, but optimizing the assembly of most of these components. In this work, a temporary test-setup of Medusa was used for high-resolution tomography of a sandstone, achieving a spatial resolution of 0.86 μm . During these experiments, Medusa was equipped with the Varian PaxScan detector of the dual-head system and an X-Ray WorX THC transmission X-ray tube.

HECTOR

HECTOR stands for 'Higher Energy CT Optimized for Research' and may be considered as the working horse of the UGCT (figure 2.10). Hector is equipped with an X-RAY WorX directional X-ray tube, which can operate at a voltage of up to 240 keV and a power of maximum 280 W. The resolution limit of the system is $\sim 3 - 4 \mu\text{m}$. The detector of Hector is a PerkinELmer 1620 CN3 CS large flat panel detector. The detector has a 2048 by 2048 pixel resolution, a pixel size of 200 by 200 μm and an absolute size of 41 by 41 cm. The entire system is fixed on a large granite back plate, to ensure maximum stability. HECTOR is a highly flexible system due to its large power and voltage range, large maximum source-detector distance and strong motors, capable of manipulating up to 80 kg. Although HECTOR was specifically developed to enable researchers to image large and heavy samples (e.g. stone and concrete cores of more than 10 cm in diameter), it has become the most-used system of all of the UGCT systems. A detailed description of the system is given in Masschaele et al. (2013).

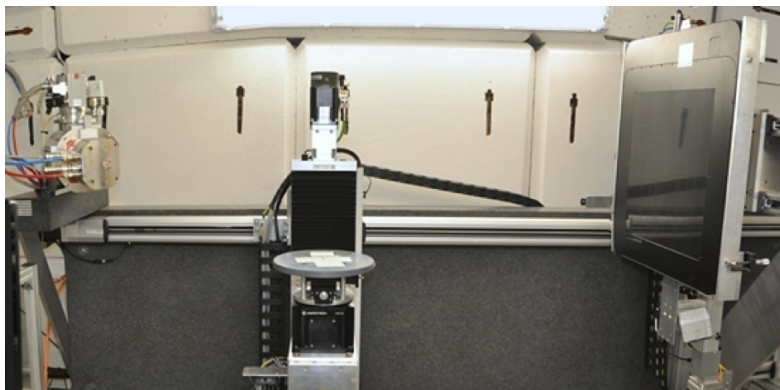


Figure 2.10: HECTOR, with a high-energy directional X-ray tube, strong rotation motor and large PerkinElmer flat panel detector.

Other setups

Apart from the three setups described above, UGCT developed three other devices that were not used for the research described in this thesis, but are worth mentioning.

Nanowood was the second UGCT system, developed in 2009, specifically

for the Laboratory for Wood Technology (WoodLab) of Ghent University. It was designed to image both large (several tens of cm) and very small (<1 mm) samples. The system therefore has two tubes and two detectors, and switching between two different configurations can be done fully automatic. Like in the dual-head system, there is a directional tube (Hamamatsu L9181, max voltage 130 kV, max power 35 W, spot size 5 μm) and a nano-focus transmission tube (Hamamatsu L1711) with a minimum spot size of 400 nm. The two detectors are a Varian PaxScan 2520V (identical to the one on the dual-head system) and an air-cooled PhotonicScience VHR CCD camera (3600 x 3200 px) for high resolution imaging of low-attenuating (organic) samples. More information about the Nanowood system can be found in Dierick et al. (2014).

The EMCT, or *Environmental CT* scanner is unique in the sense that the sample remains fixed, and the tube and detector rotate around it, much like in a medical CT system. Unlike in a medical scanner, the gantry system allows for changing the geometrical magnification, with a maximum spatial resolution of 5 μm . The EMCT was designed to image samples or setups where rotation is complicated, e.g. flow or compression cells with wires and tubes attached. Furthermore, combined with the high maximum rotation speeds (up to 5 RPM), the setup is ideal for imaging of dynamic processes such as two-phase fluid flow, elastic compression or crack propagation. The source of the EMCT is a Hamamatsu L9181 directional tube (identical to Nanowood's directional tube) and a Xineos-1313 high speed CMOS flat-panel detector (1300 x 1300 px; 100 μm pixel size) is mounted. This type of detector is perfect for fast dynamic imaging due to high readout speeds.

2.4.2 Software packages developed at the UGCT

Reconstruction software: Octopus

Octopus Reconstruction (Vlassenbroeck et al., 2007) is a reconstruction package developed at the UGCT, and is currently distributed by Inside Matters. Octopus Reconstruction is able to obtain a high reconstruction speed using GPU implementations, can correct for a lot of geometrical misalignments of the acquisition setup and evaluate these corrections on a single slice. Octopus Reconstruction uses a straight-forward and user-friendly workflow, making it a very accessible software package. All μCT reconstructions in this work are performed with Octopus.

Analysis software: Octopus Analysis / Morpho+

Octopus Analysis (OA) is a software package for 3D image analysis, originally developed as Morpho+ by the UGCT (Brabant et al., 2011) and is currently distributed by Inside Matters. OA is developed to be a very user-friendly package capable of handling large datasets in a reasonable amount of time. Morpho+ uses a fixed workflow that is easily understood by advanced and beginning users, that consists out of image filtering, segmentation, binary operations and particle analysis.

2.5 Summary

μ CT has developed into a highly flexible and reliable method to image the internal structure of porous materials. The method has grown from an expensive technique with limited availability to a fast and widely accessible one, with thousands of experts around the world. Using μ CT, features with sizes from below 1 μm to several centimetres can be investigated and measured in three dimensions. This flexibility and multi-scale possibilities make it an excellent technique for the subject of this thesis.

References

- S. Alkan, Y. Zhang, and F. Lam. Moisture Distribution Changes and Wetwood Behavior in Subalpine Fir Wood during Drying Using High X-Ray Energy Industrial CT Scanner. *Drying Technology*, 25(3):483–488, mar 2007. ISSN 0737-3937. doi: 10.1080/07373930601184023.
- C.H. Arns, F. Bauget, A. Limaye, A. Sakellariou, T. J. Senden, A. P. Sheppard, R. M. Sok, W. V. Pinczewski, S. Bakke, L. I. Berge, P-E Øren, and M A Knackstedt. Pore-scale characterization of carbonates using X-ray microtomography. *Spe Journal*, 10(4):475–484, 2005.
- J. Baruchel, J-Y. Buffiere, P. Cloetens, M. Di Michiel, E. Ferrie, W. Ludwig, E. Maire, and L. Salvo. Advances in synchrotron radiation microtomography. *Scripta Materialia*, 55(1):41–46, jul 2006. ISSN 13596462. doi: 10.1016/j.scriptamat.2006.02.012.
- S. C. Blair, P. A. Berge, and J. G. Berryman. Using two-point correlation functions to characterize microgeometry and estimate permeabilities of sandstones and porous glass. *Journal of Geophysical Research*, 101(B9): 20359, 1996. ISSN 0148-0227. doi: 10.1029/96JB00879.
- M. A. Boone. *3D visualization of mineral carbonation: CT as a tool to understand pore scale processes*. PhD thesis, Ghent University, Belgium, 2015.
- M.N. Boone. *New imaging modalities in high resolution X-ray tomography*. PhD thesis, Ghent University, Belgium, 2014.
- A.C. Bovik, S.J. Aggarwal, F. Merchant, N.H. Kim, and K.R. Diller. Automatic area and volume measurements from digital biomedical images. In D-P Häder, editor, *Image Analysis. Methods and Applications*, pages 23–64. CRC Press, Boca Raton, 2001.
- L. Brabant, J. Vlassenbroeck, Y. De Witte, V. Cnudde, M. N. Boone, J. Dewanckele, and L. Van Hoorebeke. Three-Dimensional Analysis

- of High-Resolution X-Ray Computed Tomography Data with Morpho+. *Microscopy and Microanalysis*, 17(2):252–263, 2011. doi: 10.1017/s1431927610094389.
- F. Brun, L. Mancini, P. Kasae, S. Favretto, D. Dreossi, and G. Tromba. Pore3D: A software library for quantitative analysis of porous media. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 615(3):326–332, apr 2010. ISSN 01689002. doi: 10.1016/j.nima.2010.02.063.
- T. Bultreys, L. Van Hoorebeke, and V. Cnudde. Multi-scale, micro-computed tomography-based pore network models to simulate drainage in heterogeneous rocks. *Advances in Water Resources*, 78:36–49, apr 2015. ISSN 03091708. doi: 10.1016/j.advwatres.2015.02.003.
- V. Cnudde and M.N. Boone. High-resolution X-ray computed tomography in geosciences: A review of the current technology and applications. *Earth-Science Reviews*, 123(fufu):1–17, aug 2013. ISSN 00128252. doi: 10.1016/j.earscirev.2013.04.003.
- V. Cnudde, B. Masschaele, M. Dierick, J. Vlassenbroeck, L. Van Hoorebeke, and P. Jacobs. Recent progress in X-ray CT as a geosciences tool. *Applied Geochemistry*, 21(5):826–832, 2006. doi: DOI10.1016/j.apgeochem.2006.02.010.
- V. Cnudde, M. Boone, J. Dewanckele, M. Dierick, L. Van Hoorebeke, and P. Jacobs. 3D characterization of sandstone by means of X-ray computed tomography. *Geosphere*, 7(1):54–61, 2011. ISSN 1553-040X. doi: 10.1130/GES00563.1.
- V. Cnudde, J. Dewanckele, W. De Boever, L. Brabant, and T. De Kock. 3D characterization of grain size distributions in sandstone by means of X-ray computed tomography. In *Quantitative mineralogy and microanalysis of sediments and sedimentary rocks*, pages 99–113. 2012.
- Y. De Witte. *Improved and practically feasible reconstruction methods for high resolution X-ray tomography*. Phd. thesis, Ghent University, 2010.
- M. Dierick, D. Van Loo, B. Masschaele, J. Van den Bulcke, J. Van Acker, V. Cnudde, and Luc Van Hoorebeke. Recent micro-CT scanner developments at UGCT. *Nuclear Instruments and Methods in Physics*

- Research Section B: Beam Interactions with Materials and Atoms*, 324: 35–40, apr 2014. ISSN 0168583X. doi: 10.1016/j.nimb.2013.10.051.
- E. Espes, C. Gratorp, B. Hansson, O. Hemberg, G. A. Johansson, J. Kronstedt, M. Otendal, P. Takman, and T. Tuohimaa. Liquid-metal-jet and ultra-high resolution X-ray tube technology including imaging and diffraction applications. In *Digital Industrial Radiology and Computed Tomography*, Ghent, 2015.
- M. Firsching, M. Bohnel, G. Errmann, T.O.J. Fuchs, U. Hassler, V. Heusinger, T. Hofmann, S. Kasperl, S. Moser, N. Reims, M. Salamon, T. Schon, C. Schorr, S. Schropfer, F. Sukowski, K. Tigkos, N. Uhlmann, and R. Hanke. 3-D scanning of sea freight containers using MeV X-rays. In *Nuclear Science Symposium and Medical Imaging Conference (NSS/MIC)*, pages 1–5. IEEE, 2013. doi: <http://dx.doi.org/10.1109/NSSMIC.2013.6829526>.
- G.N. Hounsfield. Computerized transverse axial scanning (tomography): Part 1. Description of system. *British journal of radiology*, 46(552): 1016–1022, 1973.
- L-K. Huang and M-J. J. Wang. Image thresholding by minimizing the measures of fuzziness. *Pattern recognition*, 28(1):41–51, 1994.
- P. Iassonov, T. Gebrenegus, and M. Tuller. Segmentation of X-ray computed tomography images of porous materials: a crucial step for characterization and quantitative analysis of pore structures. *Water resources research*, 45(W09415):n/a–n/a, sep 2009. ISSN 00431397. doi: 10.1029/2009WR008087.
- J. Jakubek, T. Holy, M. Jakubek, D. Vavrik, and Z. Vykydal. Experimental system for high resolution X-ray transmission radiography. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 563(1):278–281, jul 2006. ISSN 01689002. doi: 10.1016/j.nima.2006.01.033.
- R. A. Ketcham and W. D. Carlson. Acquisition, optimization and interpretation of X-ray computed tomographic imagery: applications to the geosciences. *Computers & Geosciences*, 27(4):381–400, 2001.
- W. B. Lindquist and A. Venkatarangan. Investigating 3D Geometry of Porous Media from High Resolution Images. *Physics and Chemistry of the Earth*, 25(1):593–599, 1999.

- F. Longuetaud, J-M. Leban, F. Mothe, E. Kerrien, and M-O. Berger. Automatic detection of pith on CT images of spruce logs. *Computers and Electronics in Agriculture*, 44(2):107–119, aug 2004. ISSN 01681699. doi: 10.1016/j.compag.2004.03.005.
- B. Masschaele, M. Dierick, D. Van Loo, M. N. Boone, L. Brabant, E. Pauwels, Veerle Cnudde, and Luc Van Hoorebeke. HECTOR: A 240kV micro-CT setup optimized for research. *Journal of Physics: Conference Series*, 463:012012, oct 2013. ISSN 1742-6596. doi: 10.1088/1742-6596/463/1/012012.
- B.C. Masschaele, V. Cnudde, M. Dierick, P. Jacobs, L. Van Hoorebeke, and J. Vlassenbroeck. UGCT: New X-ray radiography and tomography facility. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 580(1):266–269, sep 2007. ISSN 01689002. doi: 10.1016/j.nima.2007.05.099.
- N Otsu. A threshold selection method from gray-level histograms. *IEEE Transactions on Systems, Man, and Cybernetics*, 9:62–66, 1979.
- T.W. Ridler and S. Calvard. Picture Thresholding Using an Iterative Selection Method. *IEEE Transactions on Systems, Man, and Cybernetics*, SMC-8(8):630–632, 1978.
- J.C. Russ. *The Image Processing Handbook*. CRC Press, Boca Raton, 4th edition, 2002.
- J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, C. Rueden, S. Saalfeld, B. Schmid, J-Y. Tinevez, D. J. White, V. Hartenstein, K. Eliceiri, P. Tomancak, and A. Cardona. Fiji: an open-source platform for biological-image analysis. *Nature Methods*, 9(7):676–682, 2012. doi: <http://dx.doi.org/10.1038/nmeth.2019>.
- J. A. Seibert and J. M. Boone. X-ray imaging physics for nuclear medicine technologists. Part 2: X-ray interactions and image formation. *Journal of nuclear medicine technology*, 33(1):3–18, 2005. ISSN 0091-4916. doi: 33/1/3[pil].
- M. Sezgin and B. Sankur. Survey over image thresholding techniques and quantitative performance evaluation. *Journal of electronic imaging*, 13(1):146–165, 2004.

- P. Soille. *Morphological image analysis*. Springer-Verlag, Berlin, 1999.
- S. Torquato. Statistical Description of Microstructures. *Annual Review of Materials Research*, 32(1):77–111, aug 2002. ISSN 1531-7331. doi: 10.1146/annurev.matsci.32.110101.155324.
- D. Van Loo, M. Dierick, B. Masschaele, M. Boone, J. Van Den Bulcke, V. Cnudde, J. Van Acker, and L. Van Hoorebeke. A Flexible and Modular X-ray Micro and Sub-micron CT Scanner for Multi-resolution and Interdisciplinary Research. In *ICTMS 2013*, volume 5, pages 81–84, 2013.
- L. Vincent and P. Soille. Watersheds in digital spaces: an efficient algorithm based on immersion simulations. *IEEE Transactions on Pattern Analysis and Machine Intelligence*, 13(6):583–598, jun 1991. ISSN 01628828. doi: 10.1109/34.87344.
- J. Vlassenbroeck. *Advances in laboratory-based X-ray microtomography*. PhD thesis, Ghent University, 2009.
- J. Vlassenbroeck, M. Dierick, B. Masschaele, V. Cnudde, L. Hoorebeke, and P. Jacobs. Software tools for quantification of X-ray microtomography. *Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment*, 580(1):442–445, 2007. doi: 10.1016/j.nima.2007.05.073.
- D. Wildenschild and A. P. Sheppard. X-ray imaging and analysis techniques for quantifying pore-scale structure and processes in subsurface porous medium systems. *Advances in Water Resources*, 51(0):217–246, 2013. ISSN 0309-1708. doi: <http://dx.doi.org/10.1016/j.advwatres.2012.07.018>.

3

Review of the current state of 3D imaging techniques for geological materials

3.1 Introduction

This chapter provides a review of the current state of high-end 3D image-based characterisation methods that are used for imaging of the internal structure of rocks. Of course, optical microscopy and scanning electron microscopy are the most widespread methods for this purpose, but since these techniques have already been discussed in chapter 1, no further mention of these methods will be made. Although chapter 2 was devoted to the technique of μ CT, one section in this chapter gives a detailed review of the historical and recent applications of computed tomography in geosciences. Further, two techniques that can acquire very high 3D spatial resolutions are discussed: focused ion beam nanotomography and ptychographic tomography. For all of these methods, both possibilities for structural characterisation and determination of the chemical composition are discussed. This chapter has been included in an invited review that has been submitted to Earth Science Reviews as:

Imaging and image-based fluid transport modeling at the pore scale in geological materials: a practical introduction to the current state-of-the-art. (Bultreys, T., **De Boever, W.** and Cnudde, V.). The Ph.D. candidate was responsible for this part of this review.

3.2 Applications of μ CT in geosciences

3.2.1 Porosity characterisation

Before X-ray micro-CT was developed, 3D characterisation of pores could either be done by using statistical models (Hazlett, 1997) from thin section images, or by process-based models (Øren and Bakke, 2002). Both of these methods had their advantages, but advances in X-ray technology made it possible to visualise complex pore networks in 3D, down to sub-micron scales (Brunke et al., 2007, 2010; Sakellariou et al., 2010; Sok et al., 2010). First applications of (medical) CT scanners in earth sciences were in paleontology (Conroy and Vannier, 1984) and soil science (Anderson et al., 1990; Hainsworth and Aylmore, 1989; Mooney, 2002; Petrovic et al., 1982; Warner et al., 1989). Petroleum engineers used medical CT systems for fluid-flow experiments (Geraud et al., 1998; Vinegar and Wellington, 1987; Wellington and Vinegar, 1987) and sedimentologists for the analysis of sedimentary structures. Carlson and Denison (1992) applied medical CT systems to reveal the location of garnet porphyroblasts in metamorphic rocks. Although medical CT scanners have drastically improved in terms of image quality, imaging speed and deposited radiation dose over the last decades, spatial resolution remains limited to several hundreds of micrometres, because these scanners are designed to scan large objects (patients) in a very short time. Since these early days, and especially since the rapid development of μ CT, X-ray computed tomography has been growing as one of the main characterisation techniques for porous media during the 21st century. Even before laboratory systems became available, synchrotron CT was used to study the pore structure of rocks and other materials, at micrometre resolution. Already in the 1990s, researchers like Lindquist (1999), Coles (1994) and Spanne (1994) did a lot of research on the 3D characterisation of porous media using high-resolution synchrotron images. Synchrotron radiation was used to measure not only porosity, but also coordination numbers of individual pores, minimum path lengths and throat sizes of

Fontainebleau sandstone, at a spatial resolution of around 10 μm (Spanne et al., 1994) and later, 6 μm (Lindquist and Venkatarangan, 1999). These results were made possible by the development of the first dedicated software packages, to handle over one gigabyte of data, which was overwhelming for these days. At around the same time, the first dynamic processes were analysed, using in-situ liquid saturation and scanning of core samples (Coles et al., 1994). These types of experiments will be addressed in the next chapter. Ketcham and Carlson (2001) provided a first and excellent review of early days of μCT as a geoscience tool, discussing every step in the process, from sample preparation, over hardware, to applications. More recently, as image quality improved, more complex samples and processes could be studied by μCT , both using synchrotron radiation and laboratory systems. Not only homogenous, simple sandstones are analysed nowadays, but also more complicated geological materials such as limestones and shales (Grochau et al., 2010; Tiwari et al., 2013), or unconsolidated soils (Bouckaert et al., 2009). With this better image quality, pore systems of rocks can be analysed in a quantitative way. At UGCT, laboratory-based CT is used as a powerful characterisation tool for a number of geological research subjects, including natural building stone characterisation and deterioration and reservoir characterisation. Early experiments included the visualisation of effects of water repellents and consolidants (Cnudde et al., 2004) and microstructure characterisation of both natural building stones and concrete (Cnudde et al., 2009). Through the in-house development of new, state-of-the-art and flexible systems (Dierick et al., 2014; Masschaele et al., 2007, 2013), both spatial resolution and image quality could be drastically improved, allowing very detailed analysis of different processes. X-ray CT is used along traditional petrographic analysis, using optical microscopy and SEM, to perform 3D petrography of the ferruginous sandstone from Flanders (Cnudde et al., 2011). Although μCT does not provide exact chemical information, combining grey scale μCT images, knowledge about mineral formulas, SEM images and thin section images, can often result in the identification of different mineral phases. This way, spatial distribution of different phases (e.g. quartz and glauconite, figure 3.1) can be studied in 3D (Cnudde et al., 2012, 2011).

A lot of research has been done on the weathering of building stones by UGCT researchers. Changes in porosity and pore network structure were observed during exposure of different limestones to a strong acid test (figure 3.2) (Dewanckele et al., 2014). During this process of dissolution

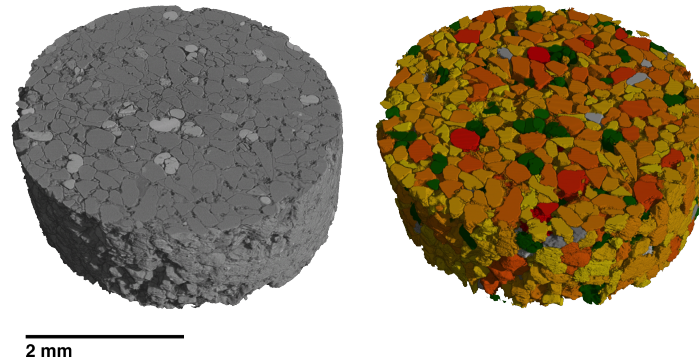


Figure 3.1: Left: 3D render of a CT-scan of the Belgian fieldstone (veldsteen). Differences in grey value can be used to separate glauconite grains (bright) from the quartz grains; Right: grain separation on the same volume. Green grains represent glauconite, quartz grains are colour coded according to size from small (yellow) to big (red) (Cnudde et al., 2012).

and recrystallization, individual pores can get disconnected or reconnected to the main pore network. Also the process of frost weathering, where fractures are created by the expanding volume of freezing water, can be monitored using X-ray CT (De Kock et al., 2013). Van Stappen et al. (2014) characterised reservoir rocks of the Kapp Toscana formation in Svalbard, Norway, to study the potential for CO₂ storage. Different samples from both reservoir cores and formation outcrops were scanned at different spatial resolutions, to characterise both big (core scale) structures and the materials microstructure. A detailed review of recent advances in high resolution X-ray CT in geosciences has been given by Cnudde and Boone (2013) and Wildenschild and Sheppard (2013).

3.2.2 Monitoring structural dynamic processes

The non-destructive character of μ CT allows the monitoring of dynamic processes inside porous media. However, in order to perform quantitative analysis, the 3D images that are taken at different moments in these processes, have to be perfectly aligned with each other (Wildenschild and Sheppard, 2013). Therefore, experiments where the sample does not have to be removed from the setup, are most convenient for dynamic imaging. This type of analysis was rapidly developed over recent years, first experiments date back to the end of the previous century (Coles et al.,

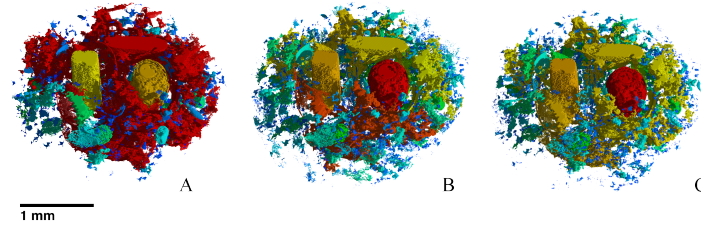


Figure 3.2: Time lapse imaging of a limestone before (A), after 10 days submission to a strong acid test (B) and after 21 days of submission to the same test (C). Each separate colour stands for a connected pore system. We can see that the pore system gets disconnected in the first stage of weathering (A-B) due to dissolution and precipitation of material. Further dissolution causes the pore system to become more connected again (B-C).

1998) (although experiments were already done using medical CAT scanners in the 1980s; Vinegar and Wellington (1987)). For improvement of results, a lot of effort is being put into the development of special sample containers (Buffière et al., 2010) that allow processes to run on the scanner setup. Dynamic CT imaging is very suited to investigate several processes, including fluid flow in porous media (Berg et al., 2013), compression of materials (Terzi et al., 2009; Voide et al., 2009) or chemical processes like corrosion of metals (Knight et al., 2010) and carbonation processes (Boone et al., 2014). Most of these experiments, especially if processes happen in a continuous way, are carried out at synchrotron facilities, since the high X-ray flux at these facilities allows for very short acquisition times, which is necessary to capture continuous processes as good as possible. Sample holders (especially if more than two consecutive scans are necessary) are typically developed with a minimum of cables attached to the sample, in order to enable rotation of the setup. Recently, Dierick et al. (2014) presented a gantry-based laboratory CT setup with stationary sample and rotating source and detector. Using this environmental CT setup, more complex sample conditioning setups can be used, and combined with high rotation speeds, dynamic processes that could previously only be analysed at synchrotron beam lines can be visualised (Bultreys et al., 2015). Obtaining a temporal resolution of 12 s, Bultreys et al. used the system to visualise drainage in Bentheim sandstone and the advection and diffusion transport of solutes in Savonnières limestone (Bultreys et al., 2015). When it is impossible (or inconvenient because of time issues) to keep the samples on the CT setup during the experiments, the images have to be aligned after each time step

and corresponding new CT scan. Unfortunately, even if samples are not removed from the sample holder, it is very challenging to reposition them in the exact same spot, since this should be done with (sub-) micrometre precision. Examples of these types of experiments are monitoring the reaction of limestone to a strong acid test (Dewanckele et al., 2012) or frost weathering (De Kock et al., 2013; Dewanckele et al., 2013), where manual image registration was performed; Derluyn et al. (2013) followed crystallization of salts in a complex limestone pore system, and image registration was performed automatically using an algorithm developed by Latham et al. (2008). Digital alignment of two 3D datasets can be done by either (rigid body) image registration, or by digital volume correlation. The first method can be used when little to no deformation of the sample has occurred, and tries to obtain a perfect voxel-to-voxel alignment. This is not as straightforward as it may seem, especially when images are scaled differently (Wildenschild and Sheppard, 2013) in terms of magnification and grey values. Image registration was first developed in 2D (Zitová and Flusser, 2003), mainly for the creation of panoramic images and remote sensing. The procedure is necessary when images are taken from different viewpoints, at different times, or by different sensors. Traditionally, 4 steps can be distinguished in image registration: feature (corresponding points in both images) detection, feature matching, transform model estimation and image resampling and transformation (Zitová and Flusser, 2003). When samples are severely deformed between different imaging steps, follow-up of processes is done by digital image (or volume) correlation (DIC, DVC). Typically, strain maps showing the vector displacement of each voxel are generated (Bay et al., 1999). These strain maps help to reveal deformation patterns that cannot be detected directly on tomographic images (Lenoir et al., 2004). Usually, strain/deformation tests are done in a triaxial test cell directly on the μ CT setup (see figure 3.3); these experiments are of great value to understand the (ductile) deformation behaviour of various materials (Lenoir et al., 2004; Viggiani et al., 2004). However, strain and crack formation can also be investigated if the load cannot be applied on the sample in situ (Zabler et al., 2008). This kind of experiments eventually lead to a better understanding of changes in rock porosity or permeability under changing reservoir conditions, and thus to a better prediction of reservoir production (Charalampidou et al., 2011; Karacan and Mitchell, 2003). For some experiments, sample cells need to be fitted with devices and probes to control temperature of the sample during experiments. Examples are CO₂

imaging in its supercritical state (Iglauer et al., 2011), where the cell needs to control temperature, pressure and flow through the sample, or analysis of snow under different temperature gradients (Schneebeli and Sokratov, 2004).

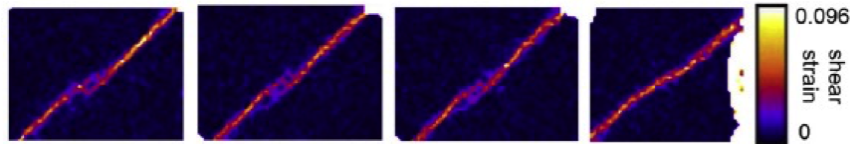


Figure 3.3: Shear strain inside a scanned sample during triaxial compression test. Adapted figure from (Charalampidou et al., 2011), with permission.

3.2.3 Phase contrast micro-tomography

Microtomography that is based on X-ray phase contrast (pc- μ CT) can be performed at synchrotron radiation facilities, and provides an X-ray technique that is up to three orders of magnitude more sensitive than conventional attenuation contrast. This makes this an ideal technique for the investigation of samples that consist out of light elements, such as organic tissues (Beckmann et al., 1997), or for samples where the attenuation contrast is very low. When heavier elements are absent, it can be problematic to distinguish features in organic samples, since the X-ray attenuation coefficient of these elements is very low. The X-ray phase contrast effect is caused by local variations of the X-ray refractive index, causing phase changes of the X-ray wave as it passes through the sample. This refraction of X-rays causes an edge-enhancing effect which is in principle an artefact, and can hinder correct segmentation of datasets (Cnudde and Boone, 2013). However, it can also be very favourable for visualisation, exposing very small structural details, even if the difference in absorption is very small or the features are very thin (Beckmann et al., 1997, 1999). This effect is mainly useful at synchrotron facilities, since it is well pronounced due to the high coherence of synchrotron radiation. Using a phase-shifting ring in the setup, resolutions down to ± 100 nm can be reached (Stampanoni et al., 2010; Langer et al., 2012). At laboratory setups designed to perform attenuation tomography, the effect mainly arises at very high resolutions and low attenuating samples (Cnudde and Boone, 2013). The amount of edge enhancement depends on

sample-detector distance, X-ray energy, detector resolution, and of course the phase properties of the sample itself (Tafforeau et al., 2006). Lak et al. (2008) and Tafforeau et al. (2006) found a valuable application of pc- μ CT in geosciences, by using the technique to study fossils. Although fossils of light elements are not usual, the chemical alterations in the fossilisation process cause very little attenuation contrast between the individual phases. An example of this kind of study is pc-CT of fossil teeth, which show no absorption contrast, due to diagenesis (all of the structures are fossilised with the same mineral composition). Pc- μ CT was used to measure enamel thickness and distribution, an important feature for paleoanthropologists (Smith et al., 2010; Tafforeau et al., 2006). On the edge between life sciences and geosciences, pc- μ CT and phase contrast radiographies are used to study fossils in amber. Especially when the amber fragments are completely opaque and the organisms (flowers, insects, spiders, etc.) are invisible in attenuation tomography, pc- μ CT is a technique with unprecedented potential (Tafforeau et al., 2006) even leading to the discovery of new species (Henderickx et al., 2006). Evidently, medicine and life sciences were among the early adopters of phase contrast radiographies and tomography; in this field, phase contrast imaging was one of the biggest changes in X-ray imaging since the invention of computed tomography (Lewis, 2004), although the technique is not a main stream and commercialised procedure yet. Early applications included the detection and visualisation of cancer lesions at the university of Tsukuba in Japan (Takeda et al., 1995, 2000). Recently, pc- μ CT has been used for the *in vivo* scanning of a fly. So-called time-resolved tomography was used, to see the actual muscle movement of this fly, whilst operating its wings (Walker et al., 2014).

An advancement in pc- μ CT is holotomography or quantitative phase microtomography. Holotomography enables imaging at good quality of materials with even smaller differences in attenuation coefficients. This way, slight variations in soft tissues or other organic matter can be imaged even better than using pc- μ CT. The method was pioneered by Peter Cloetens at the ESRF in the late 1990's (Cloetens et al., 1999). The main difference between holotomography and pc- μ CT is that holotomography uses the phase shift information acquired at different sample-detector distances for the production of phase maps (Heethof and Cloetens, 2010). Holotomography in geosciences is especially valuable in paleontology, where distinction can be made between fossilised soft tissues, e.g. to reconstruct the brain of a fossilised fish (Pradel et al., 2009).

3.3 Focused ion beam nanotomography (FIB-nt)

Over the last decades, dual-beam systems, combining a focused ion beam and an electron beam became commercially available. These systems are mainly used for the preparation of small samples, e.g. for transmission electron microscopy (Wirth, 2009) or X-ray nanotomography (Lombardo et al., 2012), but can also be used to perform a destructive type of nanotomography. Focused Ion Beam nanotomography (FIB-nt) combines an electron beam and a focused ion beam (FIB) (Bera et al., 2011; Holzer et al., 2004) to obtain the high resolutions of SEM images in three dimensions. This technique performs serial sectioning of samples using a FIB, whilst taking a SEM image after each section (figure 3.4). This series of images results in a 3D dataset of high resolution SEM images with a certain z-spacing. Due to the limitations of the FIB, the best achievable z-spacing is about 10 nm (Inkson and Möbus, 2007).

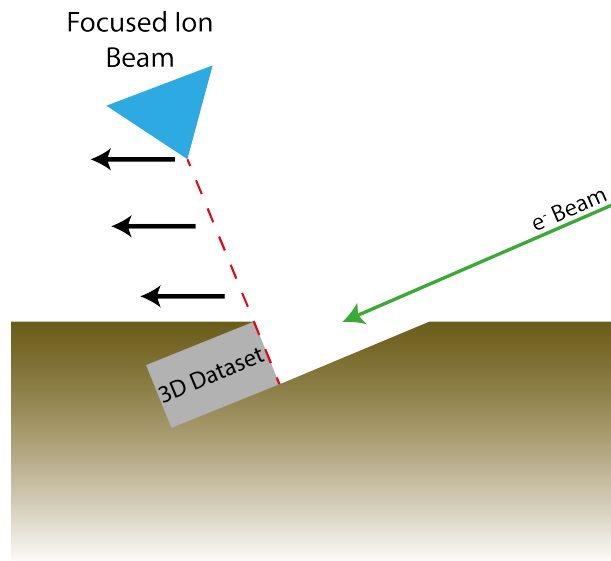


Figure 3.4: Schematic representation of FIB nanotomography. A focused ion beam sections the material, and images are taken using the electron beam. After each image, the FIB moves in the direction of the black arrows, and a new section is made.

Acquisition of FIB-nt datasets is time consuming and the analysed volume is very small (less than 10 μm in x and y direction, and usually less than 2 μm in z direction). This implies that FIB-nt can only be used for the 3D

analysis of very small regions of interest with very high detail. The destructive nature of the technique implies that dynamic processes cannot be followed on the same area of a sample, and that, especially for valuable samples, great care has to be taken during image acquisition. The technique was first presented at the end of the 1990s (Cheng, 1998; Dunn and Hull, 1999), but Holzer et al. (2004) and Wu et al. (2003) were amongst the first to demonstrate the technique on (non-geological) porous materials. Ever since, a lot of analysis has been performed on various geological materials. Recent applications include analysis of forsterite glass (De Winter et al., 2009), characterisation of clays and mudstones (Lubelli et al., 2013; Heath et al., 2011; Keller et al., 2013) and research towards the feasibility of radioactive waste storage in the Belgian Boom Clay formation (Desbois et al., 2009). FIB-nt allows the analysis of microstructures, porosity and its interconnectivity at micrometre to nanometre scale. Therefore, the technique represents a further step in the 3D analysis of rocks, complementing techniques such as X-ray tomography (chapter 2). For these reasons, FIBnt has great potential in porosity and permeability analysis, and most recent (geological) applications concern claystones and shales, to predict and improve production of natural gas from these dense types of rock (Bera et al., 2011; Jiao et al., 2014; Sok et al., 2010). This research is very important, as traditional reservoirs are getting depleted, and not much is known about these new tight gas reservoirs. Applications in the field of shale hydrocarbon reservoirs are the study of porosity in the organic matter of shales, at different thermal maturities (Curtis et al., 2012). More importantly, this organic matter porosity can only be analysed through the combined use of ion beam milling and SEM, since sample surface topography obtained by mechanical polishing tends to be higher than the diameter of most shale pores (Loucks et al., 2009). Recent applications made the technique a complementary tool to some of the most traditional geological analysis methods, as Wirth and Morales (2012) demonstrated. They analysed different samples of shale, which were sputtered with the FIB directly from standard petrographic thin sections. Sectioning normal to the thin section surface revealed a number of details that could not be observed through the optical microscope, since this technique only provided a 2D 'projection' of the 3D thin section. For example, the distribution of clay minerals, the grains of quartz, calcite and feldspar, and the development of a layering of clays wrapped around the more granular phases were evident in these trenches, but almost invisible on the thin

section surface. FIB-nt found its way in a big variety of application fields, especially in fields dealing with micro- to nanoporous media. It gave novel insights in the 3D microstructure of batteries, where permeability is of great importance for charging and discharging (Joos et al., 2011; Hutzenlaub et al., 2012). Gostovic et al. (2011) used FIB-nt to create a 3D dataset, which was then segmented into pores and solid, to serve as input for pore network extraction, giving information about connectivity and permeability of the pore system. In life sciences, FIB-nt is mainly used to study the microstructure of bones and teeth. Earl et al. (2010) could visualise and analyse the 3D shape of tubular pores inside human teeth. Giannuzzi et al. (2007) observed so called osseointegration in dental implants, which means that new bone formed into the porous wall of the implant, causing a mechanical locking mechanism at the bone/implant interface. In the study of Giannuzzi et al. (2007), FIB-nt proved to be a far more precise tool than traditional SEM microscopy, since this did not provide much information on the exact nature of this interface. Also in concrete research, FIB-nt provided new insights about morphology of pores and phases inside microporous cement pastes (Trtik et al., 2011; Munch et al., 2006). Many other applications using FIB-nt are provided in Inkson and Möbus (2007).

3.4 Ptychographic tomography

Recently, ptychographic X-ray computed tomography, provides the possibility to gather 3D structural information at nanometre scale (30 - 60 nm) resolution, be it on very small (10 - 100 μm) samples (Diaz et al., 2012; Dierolf et al., 2010). The basic principle of this technique is coherent diffractive imaging (CDI), where a monochromatic X-ray beam hits a pinhole or is focused using optics, creating a localised illumination (a few microns wide) on the sample. Unlike in scanning transmission X-ray microscopy, not only the X-ray intensity is measured by the detector, but coherent diffraction patterns of the sample (Nugent, 2010; Thibault et al., 2008). The X-ray signal is recorded in the far field. At each scan position, coherent diffraction patterns are recorded in the far field, and using iterative phase retrieval algorithms, the complex-valued transmissivity of the specimen is reconstructed (Rodenburg and Faulkner, 2004). X-ray ptychography enables resolutions of (better than) 10 nm (Schropp et al., 2012). Theoretically, the resolution of the method is only

limited by the scattering angles at which diffraction patterns can reliably be recorded, but in practice also mechanical instability and scanning accuracy affect this resolution. In ptychographic X-ray CT, 2D phase projections acquired at different angles over 180 are combined, so that a three-dimensional distribution of the electron density can be reconstructed (figure 3.5, Diaz et al. (2012); Dierolf et al. (2010)). The first demonstration of this technique came by Dierolf et al. in 2010, where a 30 μm bone sample was analysed with a $(65\text{ nm})^3$ voxel size, but resolutions up to 16 nm in 3D have been realized (Holler et al., 2014). Since 2010, experiments have been carried out in various field, for different kinds of porous and non-porous materials, including concrete (Trtik et al., 2013), textiles (Esmaili et al., 2013), carbon fibers (Diaz et al., 2014), catalysts (da Silva et al., 2015), coatings (Chen et al., 2013), solar cells (Dam et al., 2015), etc. As geological samples tend to be very resistant to the high radiation doses (typically between 10^6 to 10^9 Gy) they are exposed to during measurements, they are very well suited for ptychographic imaging. The limited size of the samples, which are generally under 50 μm in order to achieve quantitative imaging at high resolutions within reasonable time, is one of the main drawbacks of ptychographic tomography. A first application of ptychographic tomography to geological samples is given in chapter 5.

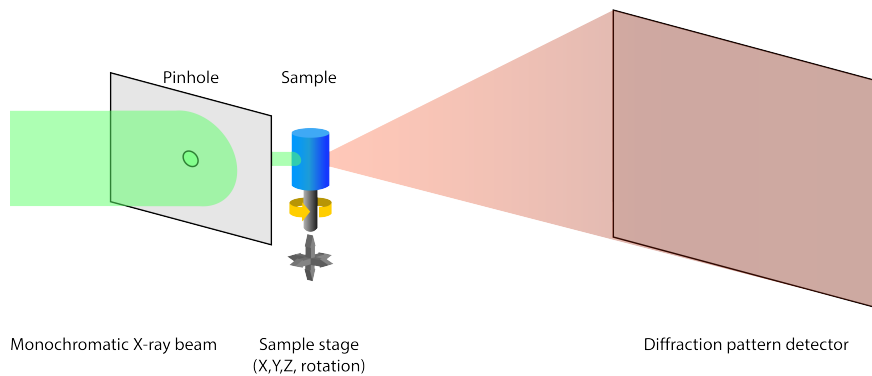


Figure 3.5: Schematic setup for ptychographic tomography. A monochromatic X-ray beam hits a pinhole (optional, this is usually not done in larger samples), and the resulting pencil beam interacts with the sample. The diffraction pattern is measured at the detector in the far field. This procedure is repeated for many spots in the samples X,Z plane, before rotating it over a small angle and repeating the entire procedure.

Ptychographic tomography produces quantitative 3D electron density maps

$n_e(r)$ of the analysed material, using the air surrounding the sample as a reference (Guizar-Sicairos et al., 2011). From these maps, the 3D mass density distribution $\rho(r)$ can be determined by:

$$\rho(r) = \frac{n_e(r)A}{N_A Z} \quad (3.1)$$

where A is the molar mass, Z is the total number of electrons in a molecule, and N_A is Avogadro's number. Because the ratio A/Z is close to 2 g/mol for most elements, the mass density can be typically measured with enough accuracy to identify some minerals in the specimen, which typically have a known density, thereby providing a 3D distribution of mineral phases with quantitative mass density values for each phase (Trtik et al., 2013).

3.5 Data fusion between different image analysis methods

Although most of the pore characterisation techniques used in this thesis are mature methods for pore space characterisation, data interpretation is still not straightforward. Each technique has its own strengths and limitations regarding resolution, reproducibility, dimensionality, cost, etc. The main challenges for the user lie in making correct assumptions and intelligent combinations between different techniques.

A first hurdle is that information in a 2D cross-section, acquired by SEM or optical microscopy, is not directly transferable to a 3D environment. This problem can be solved by using stereology, which bridges the gap between 2D planes and 3D information, by means of statistics and empirical formulas. Although valuable results were obtained using this method, it has become somewhat obsolete since the development of μ CT imaging. Since this evolution, 2D-to-3D registration was developed, in which a 2D image is aligned to its corresponding plane in the 3D volume of the same sample. This tool provides additional high-resolution 2D information directly on 3D datasets. This might be necessary when for example the spatial resolution or chemical information obtained from a CT volume is not sufficient. Since such additional information often comes from techniques that are not capable of imaging a 3D volume (SEM, EDS, etc.) merging 3D data such as CT data with 2D high resolution and/or chemical information from these techniques has become a key operation

(De Boever et al., 2015). Different methods exist for this purpose; a first method is manual alignment of the 2D data with the 3D volume. Since this is both labor-intensive and inaccurate, this is usually not the best option. Landmark based registration is a more precise way to align data acquired with different techniques onto each other. In this method, corresponding points (called landmarks) are identified manually on both the 2D and 3D images. Transformation algorithms, such as the one developed by Bookstein (Bookstein, 1989), then calculate the transformation to fit both landmark groups together, as well as the interpolation needed for the interlaying points. A more detailed workflow for this procedure is provided in chapter 4.

A final class of methods for 2D to 3D registration consists of fully automated algorithms. Although such algorithms have been developed (Latham et al., 2008), they are not yet commercially available. These registration algorithms face the difficulty of solving a transformation problem with 7 degrees of freedom: 3 translational, 3 rotational and 1 isotropic scaling. The algorithm designed by Latham et al. uses a multi-resolution search strategy, where an exhaustive low-resolution search determines an initial small set of transformation parameters. The objective is that these initial parameters bring the image already in a global minimum of deviation with reference to the target volume, and are used as starting values for an optimization method, looking for the local minimum. These values can be used to transform the 2D image to the target volume (Latham et al., 2008; Sok et al., 2010). As mentioned before, successful alignment of SEM images to CT volumes can provide additional structural information, due to the higher spatial resolution of these SEM images. This way, details about the microstructure can be linked to zones with specific grey values, corresponding to microporous regions in the CT volume.

Besides 2D-to-3D registration, aligning different volumes with each other is also an important procedure in 3D analysis. 3D-to-3D registration can be useful for multi-scale (multi-resolution) imaging, as well as for time-lapse imaging and analysis. In the first case, different volumes with different voxel sizes are fused with each other, to link high-resolution data of small volumes to bigger volumes with lower spatial resolution. In the latter case, image registration is used to be able to follow dynamic processes with voxel-size precision. Much work has been done recently to improve both forms of data fusion, and just as in 2D-to-3D registration,

registration can be performed completely manually (Dewanckele et al., 2012), which is often a time-consuming and operator-dependent analysis step. Another option to perform registration is landmark-based alignment of datasets. Ideally, registration is fully automatic, but as in 2D-to-3D registration, not many algorithms exist for complicated cases, and none are freely available (Latham et al., 2008; Sok et al., 2010). For rigid registration cases, where the sample has not changed a lot or to align overlapping datasets, algorithms are available in commercial applications such as Avizo or Dataviewer by Skyscan.

3.6 Representative elementary volume

All methods discussed in the last two chapters have certain characteristics in terms of spatial resolution and typical sample sizes. In most cases, there is a trade-off in resolution versus sample size. This trade-off can be hardware-related, as is the case for μ CT, or practical, such as for SEM, where it is impossible to image very large areas at high resolution due to time constraints. Figure 3.6 provides an overview of these limitations for the techniques that are used in this thesis. For all methods, the left side of the bar indicates maximum spatial resolution, and the right side indicates the typical sample sizes. As the image shows, μ CT has a wide distribution, but top-resolutions cannot be reached at large sample sizes. Mosaic imaging using the 2D methods of optical microscopy and SEM does have that capability, but if the highest resolutions have to be reached for very large areas, time and data management are becoming a real issue. Using FIB-nt and ptychographic tomography, the size of the analysed volume is also very small, and especially for ptychographic tomography, this issue cannot be overcome.

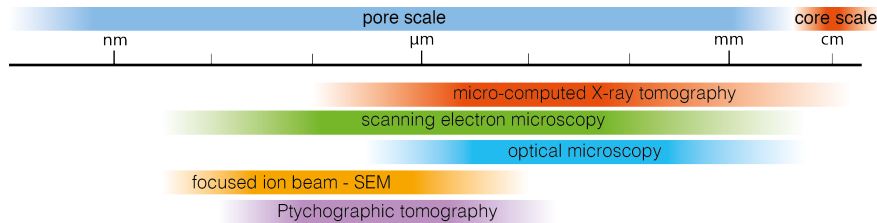


Figure 3.6: Graphical representation of the maximum resolution (left side of bars) and typical sample sizes (right side of bar) of methods used in this thesis.

Knowing that this relation between resolution and sample size exists, it is important to check if the observed area of a material is representative for this entire material in order to draw reliable and sound conclusions. The sample size at which this condition is fulfilled is called the representative elementary volume or REV. In figure 3.7, a graphical representation of the concept of the REV for porosity analysis is given. In zone 1, so-called microscopic changes effect the local measurement of porosity. At the smallest sample size, porosity will always be 100 % or 0 %, and when increasing the region of interest that is imaged, these variation will become less and less. In zone 2, REV size is reached, and moving a region of interest of this sample size across the material will have almost no effect on the result of porosity analysis. For materials that are very homogeneous, increasing the REV even further will have no effect on the porosity of a material, under the assumption that you still capture the features that are important for analysis. Heterogeneous materials will deflect away from this 'correct ' value due to changes in the structure of the material. Of course, the real REV will be limited by the fact that small details cannot be captured at larger samples, and a well-thought decision needs to be made if either the size of the volume or the ability to image small volumes is the most important. Furthermore, the REV only counts for one particular parameter. The REV of porosity can be different from the REV for e.g. chemical composition or permeability.

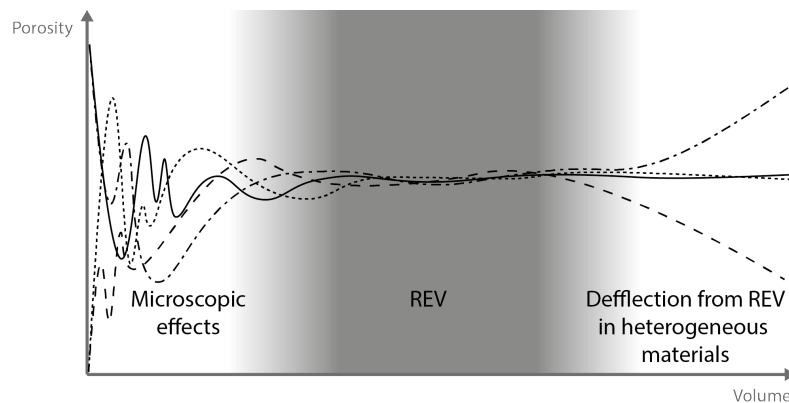


Figure 3.7: Graphical representation of the concept of the REV. For very small volumes, microscopic effects make the porosity change a lot between different measurements. At REV size, moving the analysed volume has little effect on the porosity result. At larger volumes, the result can change again due to inhomogeneities of the medium.

References

- S.H. Anderson, R.L. Peyton, and C.J. Gantzer. Evaluation of constructed and natural soil macropores using X-ray computed tomography. *Geoderma*, 46:13–29, 1990. ISSN 00167061. doi: 10.1016/0016-7061(90)90004-S.
- B. K. Bay, T. S. Smith, D. P. Fyhrie, and M. Saad. Digital volume correlation: Three-dimensional strain mapping using X-ray tomography. *Experimental Mechanics*, 39(3):217–226, sep 1999. ISSN 0014-4851. doi: 10.1007/BF02323555.
- F. Beckmann, U. Bonse, F. Busch, and O. Günnewig. X-ray microtomography (CT) Using Phase Contrast for the Investigation of Organic Matter. *Journal of Computer Assisted Tomography*, 21(4):539–553, 1997.
- F. Beckmann, K. Heise, B. Kölsch, U. Bonse, M. F. Rajewsky, M. Bartscher, and T. Biermann. Three-dimensional imaging of nerve tissue by x-ray phase-contrast microtomography. *Biophysical journal*, 76(1 Pt 1):98–102, jan 1999. ISSN 0006-3495. doi: 10.1016/S0006-3495(99)77181-X.
- B. Bera, S. K. Mitra, and D. Vick. Understanding the micro structure of Berea Sandstone by the simultaneous use of micro-computed tomography (micro-CT) and focused ion beam-scanning electron microscopy (FIB-SEM). *Micron*, 42(5):412–418, 2011. doi: 10.1016/j.micron.2010.12.002.
- S. Berg, H. Ott, S. A. Klapp, A. Schwing, R. Neiteler, N. Brussee, A. Makurat, L. Leu, F. Enzmann, J-O. Schwarz, M. Kersten, S. Irvine, and M. Stampanoni. Real-time 3D imaging of Haines jumps in porous media flow. *Proceedings of the National Academy of Sciences of the United States of America*, 110(10):3755–9, mar 2013. ISSN 1091-6490. doi: 10.1073/pnas.1221373110.

- F.L. Bookstein. Size and shape spaces for landmark data in two dimensions. *Statistical Science*, 1(2):181–242, 1989.
- M. A. Boone, P. Nielsen, T. De Kock, M. N. Boone, M. Quaghebeur, and V. Cnudde. Monitoring of stainless-steel slag carbonation using X-ray computed microtomography. *Environmental Science and Technology*, 48:674–680, 2014. ISSN 0013936X. doi: 10.1021/es402767q.
- L Bouckaert, D Van Loo, S Sleutel, S De Neve, P Jacobs, and L Van Hoorebeke. Application of X-ray tomography for quantification of the soil pore structure and visualization of soil organic matter. *Geochimica Et Cosmochimica Acta*, 73(13):A145–A145, 2009.
- O. Brunke, D. Neuber, and D. K. Lehmann. NanoCT: visualizing of internal 3D-structures with submicrometer resolution. In *Materials Research Society Symposium: Materials, Processes, Integration and Reliability in Advanced Interconnects for Micro- and Nanoelectronics*, pages 325–331, San Francisco, CA,, 2007. Materials Research Society.
- O Brunke, J Santillan, and A Suppes. Precise 3D Dimensional Metrology Using High Resolution X-Ray Computed Tomography (-ct). In S R Stock, editor, *Developments in X-Ray Tomography Vii*, volume 7804. Spie-Int Soc Optical Engineering, Bellingham, 2010. ISBN 0277-786X 978-0-81948-300-3. doi: 10.1117/12.861354.
- J. Y. Buffière, E. Maire, J. Adrien, J. P. Masse, and E. Boller. In Situ Experiments with X ray Tomography: an Attractive Tool for Experimental Mechanics. *Experimental Mechanics*, 50(3):289–305, jan 2010. ISSN 0014-4851. doi: 10.1007/s11340-010-9333-7.
- T. Bultreys, M. A. Boone, M. N. Boone, T. De Schryver, B. Masschaele, L. Van Hoorebeke, and V. Cnudde. Fast laboratory-based micro-computed tomography for pore-scale research: illustrative experiments and perspectives on the future. *Advances in Water Resources*, may 2015. ISSN 03091708. doi: 10.1016/j.advwatres.2015.05.012.
- W D Carlson and C Denison. Mechanisms of Porphyroblast Crystallization: Results from High-Resolution Computed X-ray Tomography. *Science (New York, N.Y.)*, 257:1236–1239, 1992. ISSN 0036-8075. doi: 10.1126/science.257.5074.1236.
- E-M. Charalampidou, S. A. Hall, S. Stanchits, H. Lewis, and G. Viggiani. Characterization of shear and compaction bands in a porous sandstone

- deformed under triaxial compression. *Tectonophysics*, 503(1-2):8–17, apr 2011. ISSN 00401951. doi: 10.1016/j.tecto.2010.09.032.
- B. Chen, M. Guizar-Sicairos, G. Xiong, L. Shemilt, A. Diaz, J. Nutter, N. Burdet, S. Huo, J. Mancuso, A. Monteith, F. Vergeer, A. Burgess, and I. Robinson. Three-dimensional structure analysis and percolation properties of a barrier marine coating. *Scientific reports*, 3:1177, jan 2013. ISSN 2045-2322. doi: 10.1038/srep01177.
- Z. Cheng. Development of ion and electron dual focused beam apparatus for high spatial resolution three-dimensional microanalysis of solid materials. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures*, 16(4):2473, jul 1998. ISSN 0734211X. doi: 10.1116/1.590193.
- P. Cloetens, W. Ludwig, J. Baruchel, D. Van Dyck, J. Van Landuyt, J. P. Guigay, and M. Schlenker. Holotomography: Quantitative phase tomography with micrometer resolution using hard synchrotron radiation x rays. *Applied Physics Letters*, 75(19):2912, 1999. ISSN 00036951. doi: 10.1063/1.125225.
- V. Cnudde and M.N. Boone. High-resolution X-ray computed tomography in geosciences: A review of the current technology and applications. *Earth-Science Reviews*, 123(fufu):1–17, aug 2013. ISSN 00128252. doi: 10.1016/j.earscirev.2013.04.003.
- V. Cnudde, J-P. Cnudde, C. Dupuis, and P.J.S. Jacobs. X-ray micro-CT used for the localization of water repellents and consolidants inside natural building stones. *Materials Characterization*, 53(2-4):259–271, 2004. doi: DOI10.1016/j.matchar.2004.08.011.
- V. Cnudde, A. Cwirzen, B. Masschaele, and P.J.S. Jacobs. Porosity and microstructure characterization of building stones and concretes. *Engineering Geology*, 103(3-4):76–83, feb 2009. ISSN 00137952. doi: 10.1016/j.enggeo.2008.06.014.
- V. Cnudde, J. Dewanckele, M. A. Boone, M. N. Boone, T. De Kock, L. Brabant, M. Duser, M. de Ceukelaire, H. de Clercq, R. Hayen, and P.J.S. Jacobs. High-Resolution X-Ray CT for 3D Petrography of Ferruginous Sandstone for an Investigation of Building Stone Decay. *Microscopy Research and Technique*, 74(11):1006–1017, 2011. doi: 10.1002/jemt.20987.

- V. Cnudde, J. Dewanckele, W. De Boever, L. Brabant, and T. De Kock. 3D characterization of grain size distributions in sandstone by means of X-ray computed tomography. In *Quantitative mineralogy and microanalysis of sediments and sedimentary rocks*, pages 99–113. 2012.
- M. E. Coles, P. Spanne, E. L. Muegge, and K. W. Jones. Computed microtomography of reservoir core samples. *1994 International Symposium of the Society of Core Analysts, Proceedings*, pages 9–&, 1994.
- M. E. Coles, R. D. Hazlett, P. Spanne, W. E. Soll, E. L. Muegge, and K. W. Jones. Pore level imaging of fluid transport using synchrotron X-ray microtomography. *Journal of Petroleum Science and Engineering*, - 19 (- 1-2):55–63, 1998.
- G. C. Conroy and M. W. Vannier. Non-invasive three-dimensional computer imaging of matrix-filled fossil skulls by high-resolution computed tomography. *Science (New York, N.Y.)*, 226:456–458, 1984. ISSN 0036-8075. doi: 10.1126/science.226.4673.456.
- M. E. Curtis, B. J. Cardott, C. H. Sondergeld, and C. S. Rai. Development of organic porosity in the Woodford Shale with increasing thermal maturity. *International Journal of Coal Geology*, 103:26–31, dec 2012. ISSN 01665162. doi: 10.1016/j.coal.2012.08.004.
- J. C. da Silva, K. Mader, M. Holler, D. Haberthür, A. Diaz, M. Guizar-Sicairos, W-C. Cheng, Y. Shu, J. Raabe, A. Menzel, and J. A. van Bokhoven. Assessment of the 3 D Pore Structure and Individual Components of Preshaped Catalyst Bodies by X-Ray Imaging. *ChemCatChem*, 7(3):413–416, 2015. ISSN 18673880. doi: 10.1002/cctc.201402925.
- H.F. Dam, T. R. Andersen, E. B. L. Pedersen, K. T. S. Thydén, M. Helgesen, J. E. Carlé, P. S. Jørgensen, Juliane Reinhardt, Roar R. Søndergaard, Mikkel Jørgensen, Eva Bundgaard, Frederik C. Krebs, and Jens W. Andreasen. Enabling Flexible Polymer Tandem Solar Cells by 3D Ptychographic Imaging. *Advanced Energy Materials*, 5(1):n/a–n/a, 2015. ISSN 16146832. doi: 10.1002/aenm.201400736.
- W. De Boever, H. Derluyn, D. Van Loo, L. Van Hoorebeke, and V. Cnudde. Data-fusion of high resolution X-ray CT, SEM and EDS for 3D and pseudo-3D chemical and structural characterization of sandstone. *Micron*, apr 2015. ISSN 09684328. doi: 10.1016/j.micron.2015.04.003.

- T. De Kock, M. A. Boone, J. Dewanckele, W. De Boever, M. N. Boone, G. De Schutter, and E. Lehmann. Monitoring frost susceptibility of limestone faces. In *12th International Congress on the Deterioration and Conservation of Stone*, 2013.
- H. Derluyn, M. Griffa, D. Mannes, I. Jerjen, J. Dewanckele, P. Vontobel, a. Sheppard, D. Derome, V. Cnudde, E. Lehmann, and J. Carmeliet. Characterizing saline uptake and salt distributions in porous limestone with neutron radiography and X-ray micro-tomography. *Journal of Building Physics*, 36(4):353–374, jan 2013. ISSN 1744-2591. doi: 10.1177/1744259112473947.
- G. Desbois, J. L. Urai, and P. A. Kukla. Morphology of the pore space in claystones evidence from BIB / FIB ion beam sectioning and cryo-SEM observations. *electronic Earth Discussions*, 4:1–19, 2009.
- J. Dewanckele, T. De Kock, M. A. Boone, V. Cnudde, L. Brabant, M. N. Boone, G. Fronteau, L. Van Hoorebeke, and P. Jacobs. 4D imaging and quantification of pore structure modifications inside natural building stones by means of high resolution X-ray CT. *Science of the Total Environment*, 416:436–448, 2012. doi: 10.1016/j.scitotenv.2011.11.018.
- J. Dewanckele, M. A. Boone, T. De Kock, W. De Boever, L. Brabant, M. N. Boone, G. Fronteau, J. Dils, L. Van Hoorebeke, P. Jacobs, and V. Cnudde. Holistic approach of pre-existing flaws on the decay of two limestones. *Science of the Total Environment*, 447:403–414, 2013. ISSN 00489697. doi: 10.1016/j.scitotenv.2012.12.094.
- J. Dewanckele, T. De Kock, G. Fronteau, H. Derluyn, P. Vontobel, M. Dierick, L. Van Hoorebeke, P. Jacobs, and V. Cnudde. Neutron radiography and X-ray computed tomography for quantifying weathering and water uptake processes inside porous limestone used as building material. *Materials Characterization*, 88:86–99, feb 2014. ISSN 10445803. doi: 10.1016/j.matchar.2013.12.007.
- A. Diaz, P. Trtik, M. Guizar-Sicairos, A. Menzel, P. Thibault, and O. Bunk. Quantitative x-ray phase nanotomography. *Physical Review B*, 85(2): 020104, jan 2012. ISSN 1098-0121. doi: 10.1103/PhysRevB.85.020104.
- A. Diaz, M. Guizar-Sicairos, A. Poeppel, A. Menzel, and O. Bunk. Characterization of carbon fibers using X-ray phase nanotomography. *Carbon*, 67:98–103, feb 2014. ISSN 00086223. doi: 10.1016/j.carbon.2013.09.066.

- M. Dierick, D. Van Loo, B. Masschaele, J. Van den Bulcke, J. Van Acker, V. Cnudde, and Luc Van Hoorebeke. Recent micro-CT scanner developments at UGCT. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 324: 35–40, apr 2014. ISSN 0168583X. doi: 10.1016/j.nimb.2013.10.051.
- M. Dierolf, A. Menzel, P. Thibault, P. Schneider, C. M. Kewish, R. Wepf, O. Bunk, and Franz Pfeiffer. Ptychographic X-ray computed tomography at the nanoscale. *Nature*, 467(7314):436–9, sep 2010. ISSN 1476-4687. doi: 10.1038/nature09419.
- D. N. Dunn and R. Hull. Reconstruction of three-dimensional chemistry and geometry using focused ion beam microscopy. *Applied Physics Letters*, 75(21):3414, 1999. ISSN 00036951. doi: 10.1063/1.125311.
- J. S. Earl, R. K. Leary, J. S. Perrin, R. Brydson, J. P. Harrington, K. Markowitz, and S J Milne. Characterization of dentine structure in three dimensions using FIB-SEM. *Journal of microscopy*, 240(1):1–5, oct 2010. ISSN 1365-2818. doi: 10.1111/j.1365-2818.2010.03396.x.
- M. Esmaeili, J. B. Fløystad, A. Diaz, K. Høydalsvik, M. Guizar-Sicairos, J. W. Andreasen, and D. W. Breiby. Ptychographic X-ray Tomography of Silk Fiber Hydration. *Macromolecules*, 46(2):434–439, jan 2013. ISSN 0024-9297. doi: 10.1021/ma3021163.
- Y. Geraud, F. Mazerolle, S. Raynaud, and P. Lebon. Crack location in granitic samples submitted to heating, low confining pressure and axial loading. *Geophysical Journal International*, 133(3):553–567, 1998. doi: 10.1046/j.1365-246X.1998.00471.x.
- L. A. Giannuzzi, D. Phifer, N. J. Giannuzzi, and M. J. J Capuano. Two-dimensional and 3-dimensional analysis of bone/dental implant interfaces with the use of focused ion beam and electron microscopy. *Journal of oral and maxillofacial surgery : official journal of the American Association of Oral and Maxillofacial Surgeons*, 65(4):737–47, apr 2007. ISSN 0278-2391. doi: 10.1016/j.joms.2006.10.025.
- D. Gostovic, N. J. Vito, K. A. O'Hara, K. S. Jones, and E. D. Wachsman. Microstructure and Connectivity Quantification of Complex Composite Solid Oxide Fuel Cell Electrode Three-Dimensional Networks. *Journal of the American Ceramic Society*, 94(2):620–627, feb 2011. ISSN 00027820. doi: 10.1111/j.1551-2916.2010.04111.x.

- M. H. Grochau, E. Campos, D. Nadri, T. M. Muumlmler, B. Clennell, and B. Gurevich. Sedimentary cyclicity from X-ray CT images in Campos Basin, offshore Brazil. *Leading Edge*, 29(7):808–813, 2010. doi: 10.1190/1.3462783.
- M. Guizar-Sicairos, A. Diaz, M. Holler, M. S. Lucas, A. Menzel, R. A. Wepf, and Oliver Bunk. Phase tomography from x-ray coherent diffractive imaging projections. *Optics Express*, 19(22):21345, 2011. ISSN 1094-4087. doi: 10.1364/OE.19.021345.
- J. M. Hainsworth and L. A. G. Aylmore. Non-Uniform Soil Water Extraction by Plant Roots. *Plant and Soil*, 113, 1989.
- R. D. Hazlett. Statistical characterization and stochastic modeling of pore networks in relation to fluid flow. *Mathematical Geology*, 29(6):801–822, 1997. doi: 10.1007/bf02768903.
- J. E. Heath, T. a. Dewers, B. J. O. L. McPherson, R. Petrusak, T. C. Chidsey, a. J. Rinehart, and P. S. Mozley. Pore networks in continental and marine mudstones: Characteristics and controls on sealing behavior. *Geosphere*, 7(2):429–454, mar 2011. ISSN 1553-040X. doi: 10.1130/GES00619.1.
- M. Heethof and P. Cloetens. A comparison of synchrotron X-ray phase contrast tomography and holotomography for non-invasive investigations of the internal anatomy of mites. *Soil Organisms*, 82(3): 301–316, 2010.
- H. Henderickx, P. Tafforeau, and C. Soriano. Phase-contrast synchrotron microtomography reveals the morphology of a partially visible new *Pseudogarypus* in Baltic amber (Pseudoscorpiones: Pseudogarypidae).
- Hans Henderickx, Veerle Cnudde, Bert Masschaele, Manuel Dierick, Jelle Vlassenbroeck, and Luc Van Hoorebeke. Description of a new fossil *Pseudogarypus* (Pseudoscorpiones : Pseudogarypidae) with the use of X-ray micro-CT to penetrate opaque amber. *Zootaxa*, (1305):41–50, 2006.
- M. Holler, A. Diaz, M. Guizar-Sicairos, P. Karvinen, E. Färm, E. Härkönen, M. Ritala, A. Menzel, J. Raabe, and O. Bunk. X-ray ptychographic computed tomography at 16 nm isotropic 3D resolution. *Scientific reports*, 4:3857, jan 2014. ISSN 2045-2322. doi: 10.1038/srep03857.
- L. Holzer, F. Indutnyi, P. H. Gasser, B. Münch, and M. Wegmann. Three-dimensional analysis of porous BaTiO₃ ceramics using FIB

- nanotomography. *Journal of microscopy*, 216(Pt 1):84–95, oct 2004. ISSN 0022-2720. doi: 10.1111/j.0022-2720.2004.01397.x.
- T. Hutzenlaub, S. Thiele, R. Zengerle, and C. Ziegler. Three-Dimensional Reconstruction of a LiCoO₂ Li-Ion Battery Cathode. *Electrochemical and Solid-State Letters*, 15(3):A33, 2012. ISSN 10990062. doi: 10.1149/2.002203esl.
- S. Iglauer, A. Paluszny, C. H. Pentland, and M. J. Blunt. Residual CO₂ imaged with X-ray micro-tomography. *Geophysical Research Letters*, 38(21):n/a–n/a, nov 2011. ISSN 00948276. doi: 10.1029/2011GL049680.
- B. J. Inkson and G. Möbus. Nanoscale tomography in materials science. *Materials Today*, 10(12):18–25, 2007.
- K. Jiao, S. Yao, C. Liu, Y. Gao, H. Wu, M. Li, and Z. Tang. The characterization and quantitative analysis of nanopores in unconventional gas reservoirs utilizing FESEMFIB and image processing: An example from the lower Silurian Longmaxi Shale, upper Yangtze region, China. *International Journal of Coal Geology*, 128-129: 1–11, aug 2014. ISSN 01665162. doi: 10.1016/j.coal.2014.03.004.
- J. Joos, T. Carraro, A. Weber, and E. Ivers-Tiffée. Reconstruction of porous electrodes by FIB/SEM for detailed microstructure modeling. *Journal of Power Sources*, 196(17):7302–7307, sep 2011. ISSN 03787753. doi: 10.1016/j.jpowsour.2010.10.006.
- C. Özgen Karacan and Gareth D. Mitchell. Behavior and effect of different coal microlithotypes during gas transport for carbon dioxide sequestration into coal seams. *International Journal of Coal Geology*, 53(4):201–217, mar 2003. ISSN 01665162. doi: 10.1016/S0166-5162(03)00030-2.
- L. M. Keller, P. Schuetz, R. Erni, M. D. Rossell, F. Lucas, P. Gasser, and L. Holzer. Characterization of multi-scale microstructural features in Opalinus Clay. *Microporous and Mesoporous Materials*, 170:83–94, apr 2013. ISSN 13871811. doi: 10.1016/j.micromeso.2012.11.029.
- R. A. Ketcham and W. D. Carlson. Acquisition, optimization and interpretation of X-ray computed tomographic imagery: applications to the geosciences. *Computers & Geosciences*, 27(4):381–400, 2001.
- S.P. Knight, M. Salazaras, a.M. Wythe, F. De Carlo, a.J. Davenport, and a.R. Trueman. In situ X-ray tomography of intergranular corrosion of

- 2024 and 7050 aluminium alloys. *Corrosion Science*, 52(12):3855–3860, dec 2010. ISSN 0010938X. doi: 10.1016/j.corsci.2010.08.026.
- M Lak, D Neraudeau, A Nel, P Cloetens, V Perrichot, and P Tafforeau. Phase contrast X-ray synchrotron imaging: Opening access to fossil inclusions in opaque amber. *Microscopy and Microanalysis*, 14(3):251–259, 2008. doi: 10.1017/s1431927608080264.
- M. Langer, A. Pacureanu, H. Suhonen, Q. Grimal, P. Cloetens, and F. Peyrin. X-Ray Phase Nanotomography Resolves the 3D Human Bone Ultrastructure. *Plos One*, 7(8):1–7, 2012.
- S. Latham, T. Varslot, and A. Sheppard. Image Registration: Enhancing And Calibrating X-ray Micro-CT Imaging. pages 1–12, 2008.
- N. Lenoir, S. Mareello, G. Viggiani, P. Besuelle, J. Desrues, and M. Di Michiel. *X-ray micro tomography characterization of strain localization upon deviatoric loading of saturated fine-grained stiff soils*. 2004. ISBN 90-5809-666-1.
- R. A. Lewis. Medical phase contrast x-ray imaging: current status and future prospects. *Physics in Medicine and Biology*, 49(16):3573–3583, aug 2004. ISSN 0031-9155. doi: 10.1088/0031-9155/49/16/005.
- W. B. Lindquist and A. Venkatarangan. Investigating 3D Geometry of Porous Media from High Resolution Images. *Physics and Chemistry of the Earth*, 25(1):593–599, 1999.
- J. J. Lombardo, R. A. Ristau, W. M. Harris, and W. K. S. Chiu. Focused ion beam preparation of samples for X-ray nanotomography. *Journal of synchrotron radiation*, 19(Pt 5):789–96, sep 2012. ISSN 1600-5775. doi: 10.1107/S0909049512027252.
- R. G. Loucks, R. M. Reed, S. C. Ruppel, and D. M. Jarvie. Morphology, Genesis, and Distribution of Nanometer-Scale Pores in Siliceous Mudstones of the Mississippian Barnett Shale. *Journal of Sedimentary Research*, 79(12):848–861, nov 2009. ISSN 1527-1404. doi: 10.2110/jsr.2009.092.
- B. Lubelli, D.a.M. de Winter, J.a. Post, R.P.J. van Hees, and M.R. Drury. Cryo-FIBSEM and MIP study of porosity and pore size distribution of bentonite and kaolin at different moisture contents. *Applied Clay Science*, 80-81:358–365, aug 2013. ISSN 01691317. doi: 10.1016/j.clay.2013.06.032.

- B. Masschaele, M. Dierick, D. Van Loo, M. N. Boone, L. Brabant, E. Pauwels, Veerle Cnudde, and Luc Van Hoorebeke. HECTOR: A 240kV micro-CT setup optimized for research. *Journal of Physics: Conference Series*, 463:012012, oct 2013. ISSN 1742-6596. doi: 10.1088/1742-6596/463/1/012012.
- B.C. Masschaele, V. Cnudde, M. Dierick, P. Jacobs, L. Van Hoorebeke, and J. Vlassenbroeck. UGCT: New X-ray radiography and tomography facility. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 580(1):266–269, sep 2007. ISSN 01689002. doi: 10.1016/j.nima.2007.05.099.
- S. J. Mooney. Three-dimensional visualization and quantification of soil macroporosity and water flow patterns using computed tomography. *Soil use and management*, 18:142–151, 2002. doi: 10.1079/SUM2002121.
- B. Munch, P. Gasser, L. Holzer, and R. Flatt. FIB-Nanotomography of Particulate Systems Part II: Particle Recognition and Effect of Boundary Truncation. *Journal of the American Ceramic Society*, 89(8):2586–2595, aug 2006. ISSN 0002-7820. doi: 10.1111/j.1551-2916.2006.01121.x.
- K. Nugent. Coherent methods in the X-ray sciences. *Advances in Physics*, 59(1):1–99, 2010.
- P. E. Øren and S. Bakke. Process based reconstruction of sandstones and prediction of transport properties. *Transport in Porous Media*, 46(2-3): 311–343, 2002.
- A. M. Petrovic, J. E. Siebert, and P. E. Rieke. Soil Bulk Density Analysis in Three Dimensions by Computed Tomographic Scanning. *Soil Science Society of America Journal*, 46:445–450, 1982. ISSN 0361-5995. doi: 10.2136/sssaj1982.03615995004600030001x.
- Alan Pradel, Max Langer, John G Maisey, Didier Geffard-Kuriyama, Peter Cloetens, Philippe Janvier, and Paul Tafforeau. Skull and brain of a 300-million-year-old chimaeroid fish revealed by synchrotron holotomography. *Proceedings of the National Academy of Sciences of the United States of America*, 106(13):5224–8, 2009. ISSN 1091-6490. doi: 10.1073/pnas.0807047106.
- J. M. Rodenburg and H. M. L. Faulkner. A phase retrieval algorithm for

- shifting illumination. *Applied Physics Letters*, 85(20):4795, 2004. ISSN 00036951. doi: 10.1063/1.1823034.
- A Sakellariou, A M Kingston, T K Varslot, A P Sheppard, S J Latham, R M Sok, C H Arns, T J Senden, and M A Knackstedt. Tomographic image analysis and processing to simulate micro-petrophysical experiments. In S R Stock, editor, *Developments in X-Ray Tomography VII*, volume 7804. 2010. ISBN 0277-786X 978-0-81948-300-3. doi: 10.1117/12.860293.
- M. Schneebeil and S. A. Sokratov. Tomography of temperature gradient metamorphism of snow and associated changes in heat conductivity. *Hydrological Processes*, 18(18):3655–3665, dec 2004. ISSN 0885-6087. doi: 10.1002/hyp.5800.
- a. Schropp, R. Hoppe, J. Patommel, D. Samberg, F. Seiboth, S. Stephan, G. Wellenreuther, G. Falkenberg, and C. G. Schroer. Hard x-ray scanning microscopy with coherent radiation: Beyond the resolution of conventional x-ray microscopes. *Applied Physics Letters*, 100(25):10–13, 2012. ISSN 00036951. doi: 10.1063/1.4729942.
- T. M. Smith, P. Tafforeau, D. J. Reid, J. Pouech, V. Lazzari, J. P. Zermeno, D. Guatelli-Steinberg, A. J. Olejniczak, A. Hoffman, Jakov Radovic, Masrour Makaremi, Michel Toussaint, Chris Stringer, and Jean-Jacques Hublin. Dental evidence for ontogenetic differences between modern humans and Neanderthals. *Proceedings of the National Academy of Sciences of the United States of America*, 107(49):20923–8, dec 2010. ISSN 1091-6490. doi: 10.1073/pnas.1010906107.
- R. M. Sok, T. Varslot, A. Ghous, S. Latham, A. P. Sheppard, and M. A. Knackstedt. Pore Scale Characterization of Carbonates at Multiple Scales: Integration of Micro-CT, BSEM, and FIBSEM. *Petrophysics*, 51(6):379–387, 2010.
- P Spanne, J F Thovert, C J Jacquin, W B Lindquist, K W Jones, and P M Adler. SYNCHROTRON COMPUTED MICROTOMOGRAPHY OF POROUS-MEDIA - TOPOLOGY AND TRANSPORTS. *Physical Review Letters*, 73(14):2001–2004, 1994. doi: 10.1103/PhysRevLett.73.2001.
- M. Stampanoni, R. Mokso, F. Marone, J. Vila-Comamala, S. Gorelick, P. Trtik, K. Jefimovs, and C. David. Phase-contrast tomography at the nanoscale using hard x rays. *Physical Review B*, 81(14):140105, apr 2010. ISSN 1098-0121. doi: 10.1103/PhysRevB.81.140105.

- P. Tafforeau, R. Boistel, E. Boller, a. Bravin, M. Brunet, Y. Chaimanee, P. Cloetens, M. Feist, J. Hozowska, J.-J. Jaeger, R.F. Kay, V. Lazzari, L. Marivaux, a. Nel, C. Nemoz, X. Thibault, P. Vignaud, and S. Zabler. Applications of X-ray synchrotron microtomography for non-destructive 3D studies of paleontological specimens. *Applied Physics A*, 83(2):195–202, feb 2006. ISSN 0947-8396. doi: 10.1007/s00339-006-3507-2.
- T. Takeda, A. Momose, Y. Itai, W. Jin, and K. Hirano. Phase-contrast imaging with synchrotron x-rays for detecting cancer lesions. *Academic Radiology*, 2(9):799–803, sep 1995. ISSN 10766332. doi: 10.1016/S1076-6332(05)80490-8.
- T. Takeda, A. Momose, K. Hirano, S. Haraoka, T. Watanabe, and Y. Itai. Human carcinoma: early experience with phase-contrast X-ray CT with synchrotron radiation—comparative specimen study with optical microscopy. *Radiology*, 214(1):298–301, jan 2000. ISSN 0033-8419. doi: 10.1148/radiology.214.1.r00ja08298.
- S. Terzi, L. Salvo, M. Suéry, N. Limodin, J. Adrien, E. Maire, Y. Pannier, M. Bornert, D. Bernard, and M. Felberbaum. In situ X-ray tomography observation of inhomogeneous deformation in semi-solid aluminium alloys. *Scripta Materialia*, 61(5):449–452, sep 2009. ISSN 13596462. doi: 10.1016/j.scriptamat.2009.04.041.
- P. Thibault, M. Dierolf, A. Menzel, O. Bunk, C. David, and F. Pfeiffer. High-resolution scanning x-ray diffraction microscopy. *Science (New York, N.Y.)*, 321(5887):379–82, jul 2008. ISSN 1095-9203. doi: 10.1126/science.1158573.
- P. Tiwari, M. Deo, C.L. Lin, and J.D. Miller. Characterization of oil shale pore structure before and after pyrolysis by using X-ray micro CT. *Fuel*, 107:547–554, may 2013. ISSN 00162361. doi: 10.1016/j.fuel.2013.01.006.
- P. Trtik, B. Münch, P. Gasser, A. Leemann, R. Loser, R. Wepf, and P. Lura. Focussed ion beam nanotomography reveals the 3D morphology of different solid phases in hardened cement pastes. *Journal of microscopy*, 241(3):234–42, mar 2011. ISSN 1365-2818. doi: 10.1111/j.1365-2818.2010.03433.x.
- P. Trtik, A. Diaz, M. Guizar-Sicairos, A. Menzel, and O. Bunk. Density mapping of hardened cement paste using ptychographic X-ray computed

- tomography. *Cement and Concrete Composites*, 36:71–77, feb 2013. ISSN 09589465. doi: 10.1016/j.cemconcomp.2012.06.001.
- Jeroen Van Stappen, Tim De Kock, Marijn A Boone, Snorre Olaussen, and Veerle Cnudde. Pore-scale characterisation and modelling of CO₂ flow in tight sandstones using X-ray micro-CT ; Knorringfjellet Formation of the Longyearbyen CO₂ Lab , Svalbard. *Norwegian journal of geology*, 94(November 2015):201–215, 2014.
- G Viggiani, N Lenoir, P Besuelle, M Di Michiel, S Mareello, J Desrues, and M Kretschmer. X-ray microtomography for studying localized deformation in fine-grained geomaterials under triaxial compression. *Comptes Rendus Mecanique*, 332(10):819–826, 2004. doi: 10.1016/j.crme.2004.05.006.
- H. J. Vinegar and S. L. Wellington. Tomographic imaging of three-phase flow experiments. *Review of Scientific Instruments*, 58(1):96, 1987. ISSN 00346748. doi: 10.1063/1.1139522.
- R. Voide, P. Schneider, M. Stauber, R. Wyss, M. Stampanoni, U. Sennhauser, G. H. van Lenthe, and R Muller. Time-lapsed assessment of microcrack initiation and propagation in murine cortical bone at submicrometer resolution. *Bone*, 45(2):164–173, 2009. doi: DOI10.1016/j.bone.2009.04.248.
- S. M. Walker, D. A. Schwyn, R. Mokso, M. Wicklein, T. Müller, M. Doube, M. Stampanoni, H. G. Krapp, and G. K. Taylor. In vivo time-resolved microtomography reveals the mechanics of the blowfly flight motor. *PLoS biology*, 12(3), mar 2014. ISSN 1545-7885. doi: 10.1371/journal.pbio.1001823.
- G. S. Warner, J. L. Nieber, I. D. Moore, and R. A. Geise. Characterizing Macropores in Soil by Computed Tomography, 1989.
- S. L. Wellington and H. J. Vinegar. X-ray Computerized Tomography. *Journal of Petroleum Technology*, 39(8):885–898, 1987.
- D. Wildenschild and A. P. Sheppard. X-ray imaging and analysis techniques for quantifying pore-scale structure and processes in subsurface porous medium systems. *Advances in Water Resources*, 51(0):217–246, 2013. ISSN 0309-1708. doi: <http://dx.doi.org/10.1016/j.advwatres.2012.07.018>.
- R. Wirth and L. F. Morales. Combined FIB-SEM techniques: Advanced

tools to resolve microstructures and mineral phases in sedimentary rocks. In P. Sylvester, editor, *Quantitative mineralogy and microanalysis of sediments and sedimentary rocks*, pages 17–34. 2012.

Richard Wirth. Focused Ion Beam (FIB) combined with SEM and TEM: Advanced analytical tools for studies of chemical composition, microstructure and crystal structure in geomaterials on a nanometre scale. *Chemical Geology*, 261:217–229, 2009. ISSN 00092541. doi: 10.1016/j.chemgeo.2008.05.019.

H. Z. Wu, S. G. Roberts, G. Möbus, and B. J. Inkson. Subsurface damage analysis by TEM and 3D FIB crack mapping in alumina and alumina/5vol.%SiC nanocomposites. *Acta Materialia*, 51(1):149–163, jan 2003. ISSN 13596454. doi: 10.1016/S1359-6454(02)00387-7.

S. Zabler, A. Rack, I. Manke, K. Thermann, J. Tiedemann, N. Harthill, and H. Riesemeier. High-resolution tomography of cracks, voids and microstructure in greywacke and limestone. *Journal of Structural Geology*, 30(7):876–887, jul 2008. ISSN 01918141. doi: 10.1016/j.jsg.2008.03.002.

B. Zitová and J. Flusser. Image registration methods: a survey. *Image and Vision Computing*, 21(11):977–1000, oct 2003. ISSN 02628856. doi: 10.1016/S0262-8856(03)00137-9.

4

Development of a workflow for data fusion of μ CT, SEM and EDS

This chapter describes a workflow for the combination of structural and chemical information, acquired by various two- and three-dimensional imaging techniques. A combination of μ CT and SEM-EDS was used to analyse the structure of the Vosges sandstone from sub-micron to centimetre-scale resolution. Little work had been done before on merging SEM and CT data at different resolutions at this scale, and this chapter describes a possible workflow for these kind of analyses. This chapter is based on a publication in Micron: *De Boever et al. (2015): "Data-fusion of high resolution X-ray CT, SEM and EDS for 3D and pseudo-3D chemical and structural characterisation of sandstone."* The Ph.D. candidate was the main author of this publication and did all of the analyses and experiments. Tom Bultreys and Hannelore Derluyn advised in experimental steps and co-wrote a part of the text.

4.1 Introduction

Investigation of natural stones, and the behaviour of fluids in their pore networks, is important in many scientific fields. This includes the study of reservoir rocks, which is important for the oil and gas industry (Antrett, 2013; Jiao et al., 2014), but also for hydrogeology and water management studies (Cirpka et al., 2014; Lagrou et al., 2004). Pore-scale processes, such as ice (De Kock et al., 2013; Matsuoka and Murton, 2008) or salt precipitation (Derluyn et al., 2013) and carbonation (Boone et al., 2014), also have a big influence on the weathering of building stones (Dewanckele et al., 2014), the behaviour of pavement materials, or the cracking of concrete. A full characterisation of the complex microstructure of porous media is thus of vital importance to understand and predict the processes regulating the phenomena mentioned above. For many of the materials that are common in these research fields, one main difficulty to overcome is the multi-scale character of their structure. Geological materials are composed of a mixture of macro- to micro- and even nano-scale features. Furthermore, their composition is very heterogeneous and can vary drastically over a distance of just centimetres. These inhomogeneous characteristics make it very difficult to find and combine techniques that can analyse samples over different length scales, since it is often of interest to analyse centimetre-scale samples at nanometre-precision. Another layer of complexity in the understanding of pore-scale processes in natural stones is that these processes are not only influenced by the pore structure, but also by the chemical composition of the material. In this work, a combination of different techniques is proposed, using a well-defined workflow, to acquire as much information as possible on the structure and composition of a sandstone sample. This chapter focuses on high resolution X-ray CT (μ CT), scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDS) (Reed, 2005) and FIB-nt (Holzer et al., 2004; Keller et al., 2011). Over the last few decades, μ CT has become an invaluable tool for the 3D characterisation of many materials, including natural stones (Cnudde and Boone, 2013; Ketcham and Carlson, 2001; Wildenschild and Sheppard, 2013). Although there are many important advantages for this technique, there are also some limitations. A first shortfall of μ CT is that high-resolution analysis always requires small samples, also in μ CT systems using magnification optics; although nanofocus X-ray tubes can have a focal spot size down to about 400 nm, this spatial resolution can

only be achieved by imaging extremely small (less than 1 mm) samples (Al-Raoush and Papadopoulos, 2010). This leads to questions about representative elementary volume (REV), particularly for heterogeneous geological samples. Second, the lack of chemical information in μ CT datasets is a big shortcoming for geologists, as this chemical information is of importance for the determination of minerals present in samples. Although a rough estimate or relative relationship between the densities and atomic number of the elements in the sample can be determined, quantitative values remain a challenge (Jussiani and Appoloni, 2014). This mineralogical information is of importance for the understanding of various processes that happen in the pore space of geological materials, including migration of (saline or acid) fluids (Derluyn et al., 2013) and dissolution and precipitation reactions (Dewanckele et al., 2014). In an effort to try to enhance the information acquired by μ CT, additional experiments using different methods can be executed. More exactly, we propose a workflow combining μ CT with 2D imaging techniques (SEM and EDS), and using image registration for a one-to-one fusion of the data. Data fusion of CT and 2D microscopy techniques was already done by Huddleston-Holmes and Ketcham (2005), proving the complementarity of both methods. Over the past decade, image quality and registration techniques have improved, and 3D registration algorithms have become accessible to researchers. SEM can provide 2D images of large surfaces, at much higher resolutions than μ CT (less than 10 nm for secondary electron images; Reed (2005)). Since images can be tiled into a mosaic image, there is no real limit to the surface that can be analysed. Combining μ CT with SEM images can improve information on microporosity and microstructure of analysed samples (Sok et al., 2010). When combined with EDS, the chemical composition can be analysed as well, to allow the visualisation of spatial distribution of different mineral phases. Other techniques, e.g. FIB-nt, can provide high-resolution (down to 5 nm; Holzer and Cantoni (2011)) structural and chemical information in 3D, albeit on very small volumes.

4.2 Material: the Vosges sandstone

For this research, a material had to be used that was heterogeneous in terms of structure and mineralogy. Due to its simplicity, Bentheim sandstone (Nijland et al., 2004) is not suited because understanding its

structure requires far less analysis. For this methodological study, a stone was required with a structure possessing a good variation between macropores ($>20\text{ }\mu\text{m}$) and micropores ($<1\text{ }\mu\text{m}$), and a significant amount of micas, clays and feldspars to ensure enough chemical variation. For these reasons, the Vosges sandstone was selected in this chapter.

4.3 Methods

A workflow was developed to combine information from μCT , SEM, EDS and FIB-nt. The base sample of the entire study was a 14 mm, cuboid Vosges sandstone sample (figure 4.1). This sample was embedded in resin to ensure mechanical strength, and polished down to $1/4\text{ }\mu\text{m}$ accuracy. The first step was a medium resolution CT scan of the entire sample, at the best spatial resolution ($9\text{ }\mu\text{m}$) possible for that sample size (figure 4.1, 1), using the HECTOR setup (Masschaele et al., 2013a) of UGCT. Next, SEM images and EDS mappings for three of the main occurring elements (silicon, potassium and iron; determined by point measurements of the characteristic X-ray spectrum) were performed on all 5 exposed surfaces of the sample (figure 4.1, 2). Thereafter, a small, 1 mm diameter cylindrical subsample was drilled out of the main sample, and scanned at high resolution ($0.86\text{ }\mu\text{m}$) using UGCT's MEDUSA setup (figure 4.1, 3). We leave the option open to perform other, higher-resolution techniques on this small microplug (at resolutions $<100\text{ nm}$), to study regions of the sample in 3D which were too fine-grained for μCT (figure 4.1, 4).

4.3.1 μCT

Image acquisition

μCT scans were performed at the UGCT. Two different setups were used, one for the medium resolution, and another one for the high resolution scans. For the medium resolution scans, HECTOR (Masschaele et al., 2013) was used. For this experiment, the source was operated at a voltage of 150 kV and a power of 10 W. 2000 projections were taken at an exposure time of 2 s. The voxel size of this dataset was $8.9\text{ }\mu\text{m}$. High-resolution CT scans were performed on the new MEDUSA setup of the UGCT, 2800 projections were taken, with an exposure time of 1.5 s.

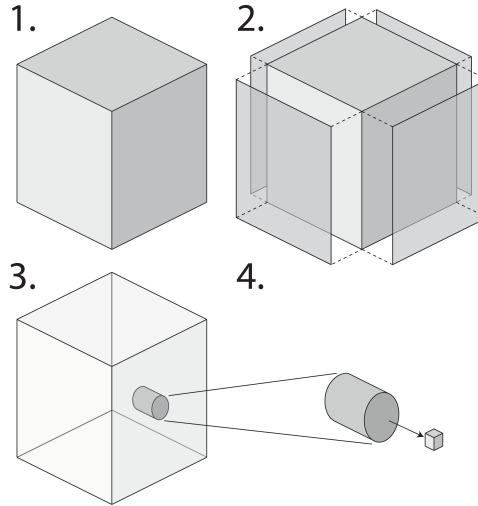


Figure 4.1: Schematic representation of the workflow for this study. 1) 14 mm sample for medium resolution CT. 2) SEM and EDS mappings of the 5 exposed sides of the sample. 3) Extraction of 1 mm diameter sub-sample for high-resolution CT. 4) Possibility of further investigation of sub-sample using other, high-resolution techniques.

The tube voltage for this experiment was 90 kV. Using these parameters, a voxel size of $0.86 \mu\text{m}$ was reached.

Reconstruction and image analysis

For the reconstruction of the raw projections, Octopus Reconstruction was used (Vlassenbroeck et al., 2007). Image analysis was done using Octopus Analysis (Brabant et al., 2011) and Avizo (www.vsg3d.com).

4.3.2 Scanning electron microscopy and energy dispersive X-ray spectroscopy

For each of the exposed surfaces of the sample (top surface and 4 lateral surfaces), a grid of SEM images was acquired to compose a photomosaic of the entire surface. The analysis was performed on a JEOL 5310-LV system, equipped with a secondary and backscattered electron detector and an Oxford Instruments silicon-drift detector for EDS analysis. A total of

300 backscattered SEM images were acquired at each plane, resulting in a total of 1500 images, which had to be taken manually since the JEOL 5310 is not equipped with automated stage control. The SEM was operated at 20 kV with a spot size of 13 nm and a working distance of 20 mm. Images were stitched together using the Microsoft Image Composite Editor (ICE; <http://research.microsoft.com>), which has algorithms for automatic grid-based registration of images. Next, EDS mappings were obtained, at 24 to 28 images per side. Due to time restrictions, only half of the surface of the SEM photomosaics was covered, at half the magnification. This resulted in 125 separate acquisitions, taking over 40 hours to acquire the data.

4.3.3 Focused ion beam nanotomography

The final method that was used in the investigation of the Vosges sandstone was FIB-nanotomography. These experiments were carried out at the department of Information Technology of Ghent University (www.fib.intec.ugent.be) using a FEI Nova Nanolab 600 Dual-beam system. FIB-nt was used to investigate regions in the sample where porosity and grains were too narrow and small to be visible on the μ CT data. This was especially the case in the fine-grained zones inside the material. The pixel size of the individual slices was 16 nm, and 200 slices were imaged, at 50 nm z-intervals. This resulted in a $17 \times 14 \times 10 \mu\text{m}^3$ volume.

4.3.4 Data fusion

Image registration was used to link the information from the different techniques. For various reasons it was very difficult to do this registration using automated algorithms: images were acquired using different techniques and different detectors, meaning that the form of corresponding features in images captured with different methods was not completely the same. This effect occurs because the angles of the 14 mm sample were not completely straight, and SEM imaging was therefore not always performed with a beam perpendicular to the sample surface. Furthermore, the direction of the CT slices in the vertical planes was never completely parallel or perpendicular to the samples surfaces. Furthermore, SEM images provide a depth of view beyond the sample surface, which is absent in 2D CT slices. This is usually an advantage of SEM imaging, but

proves to be a disadvantage for registration. To overcome these issues, landmark-based registration was employed. Corresponding points in the reference and transformed image were manually selected. The transformation to match those two point groups was then calculated and images were transformed or warped using the same transformation equation. If there was only rigid-body movement, and no deformation, a simple rigid transformation algorithm could be used to register the two images. However, due to the use of different detectors and techniques, distortion was present in the images, and an algorithm called Bookstein Image Warp (Bookstein, 1989) was used to register the images. Using this algorithm, points from the transformed group were forced to fit the reference points, and all image points in between were shifted by using correlation of the surrounding points (Bookstein, 1989). In this research, three types of registration were necessary: 2D to 2D registration to match EDS data to the SEM images, 2D to 3D registration to match these data to the 3D CT volume, and 3D to 3D registration to identify the location of the sub-sample in the base sample. In the first case, only X/Y transformation was necessary, whereas in the other cases, rotation and translation in three dimensions had to be performed.

4.4 Results

4.4.1 μ CT

The first CT scan at medium resolution (voxel size: 8.9 μm) provides a good insight regarding the distribution of dense inclusions (mostly titanium oxides), and gives an idea about the internal structure of the stone. Most of the rest of the solid matrix had about the same grey value, so there is hardly any contrast between the quartz grains and other mineral phases present (figure 4.2, left). Further, the size of the grains and of the pore system makes it impossible to perform a decent analysis of grain/pore shape and size. Image analysis with Morpho+ resulted in a porosity of 9.04 %, consisting of 5.4 % open porosity (connected to the outside of the sample) and 3.6 % closed porosity. This high amount of closed porosity is not normal for a sandstone like the Vosges sandstone (Bésuelle et al., 2000), and can only be explained by the lack of spatial resolution in the dataset. Attention has to be drawn to the high dependency of results on choices made during image segmentation. A small difference in threshold

value causes high changes in resulting porosity, meaning that the resolution of this CT scan is just not high enough for decent analysis of the sample. High resolution scanning of the 1 mm microplug (voxel size: 0.86 μm) resulted in a much better scan where porosity was clearly resolved; boundaries between porosity and grains were very sharp (figure 4.2, right), meaning that results from image segmentation can be considered reliable. Grains and pores could be segmented, and the total porosity by image analysis was found to be 16.50 %, of which only 0.2 % was characterised as closed porosity. In the high-resolution images, there was contrast between quartz grains, feldspars and micas, and dense minerals. However, contrast between quartz and feldspars, micas and clays was not enough to analyse each individual phase.

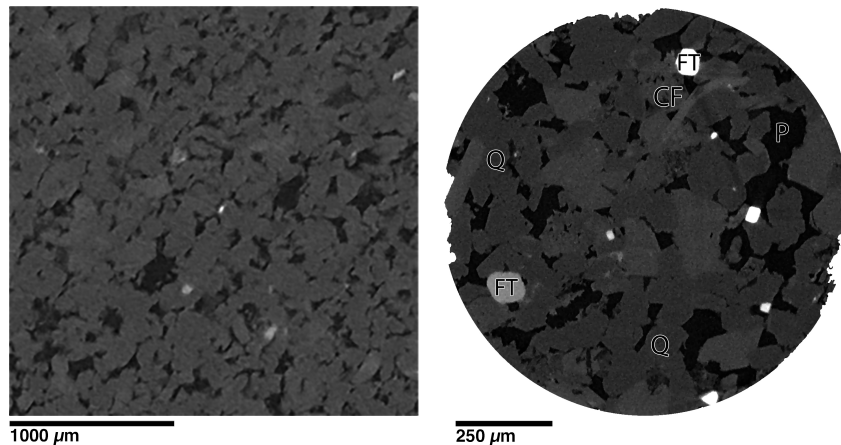


Figure 4.2: Left: detail of 2D slice from medium resolution CT scan (voxel size: 9 μm); right: 2D slice from high resolution CT scan (voxel size: 0.86 μm). Image quality is much better in the high-resolution scan, so sample analysis is much more accurate than for the low resolution scan. Annotations: Q = quartz, CF = clays and feldspars, FT = iron and titanium oxides, P = pore.

4.4.2 Scanning electron microscopy and energy dispersive X-ray spectroscopy

As a result of the SEM analysis, panoramic images of each surface of the sample were obtained. At the magnification that was used, the pixel size in the images was 1.08 μm . This is about one order of magnitude better than the resolution of the medium resolution CT scan, i.e. compared to the 8.9

μm voxel size of the CT scan of the entire sample. Contrast in the BSE images is visible between quartz and feldspars, albeit not very clear at the energy and spot size used. The dense titanium oxides show a very high contrast with respect to the other minerals, but are rather scarce in the 2D planes. EDS mappings revealed the distribution for silicon, potassium and iron. Grains which are very rich in silicon can be determined as quartz (SiO_2) grains, zones rich in potassium are feldspars (KAlSi_3O_8) or micas (e.g. muscovite: $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F,OH})_2$) and iron-rich zones are areas where iron oxides are present. The images indicate a rather uniform distribution of quartz, feldspars, micas and clay minerals throughout the entire sample; however, the iron is mainly present in a distinct layer, mainly on two of the five surfaces. It is also apparent that most of the iron is not present in the form of grains, but is often located inside the cement that binds these grains together (figure 4.3). These results prove that SEM combined with EDS gives a good idea about the presence of different mineral phases inside the investigated sample, and that EDS is still a useful tool that can reveal the presence of different mineral phases, even if there is no compositional variance visible in SEM images. Furthermore, distribution of these phases in the 2D surfaces of the material is easily observed and analysed.

4.4.3 Image registration

2D-to-2D

2D-to-2D image registration between SEM and EDS images provides grain-to-grain information about mineralogy, even when contrast in BSE images is too low (figure 4.3). Image registration was done using landmarks, which are very easy to detect, since both images have almost the same feature shape and the orientation of the images is the same. Due to the depth of view in SEM images (images show information beyond the absolute surface of the sample) it is very difficult to use automated algorithms. We remark that this step is not necessary on most modern SEM machines, as they can link SEM and EDS data automatically however it is necessary if the SEM machine is not equipped with an automated stage control, as was the case in this research. This method allows combination of SEM images with chemical information derived from other techniques as well, such as micro-X-ray fluorescence ($\mu\text{-XRF}$) (Boone et al., 2011).

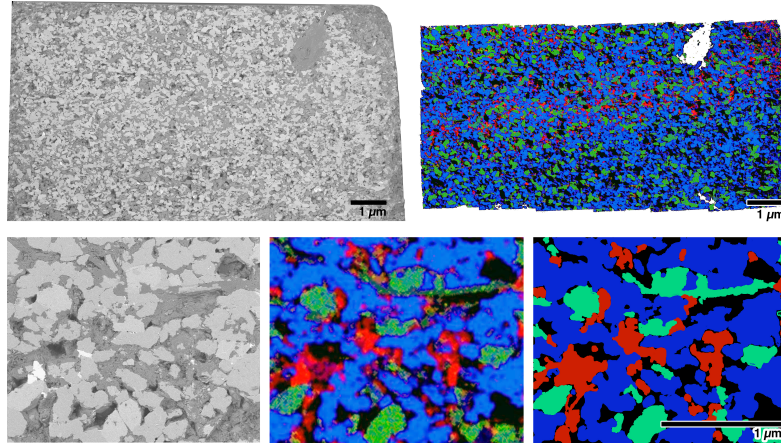


Figure 4.3: Top: SEM image and corresponding EDS map. Blue = Quartz, Green = Micas and feldspars, Red = Iron oxides. Bottom: Left: detail of SEM image; middle: detail of EDS map; right: simplified representation of EDS map. Grains can be identified individually as different minerals.

2D-to-3D

Although both CT and SEM/EDS images reveal a lot of information on the structure and mineralogy of the sample, this information becomes much more useful if the orientation and distribution of the different mineral phases can be linked directly to the low-resolution CT volume. This way, 3D orientation of certain layers can be observed and measured. After registration of the 2D SEM and EDS images to the 3D volume, we can see the orientation (figure 4.8) of the iron-rich zone that was described in the previous paragraph (figure 4.3). Although the SEM and EDS images are in 2D, this method yields a pseudo-3D look at the distribution of the iron inside the sample. 2D to 3D image registration of SEM (and EDS) images to the CT volume is not straightforward, and besides the depth of view difference, corresponding features in both image sets do not have the exact same form. This effect occurs since the angles of the 14 mm sample were not completely straight, and SEM imaging was therefore not always performed with a beam perpendicular to the sample surface. Furthermore, the direction of the CT slices in the vertical plains was never completely parallel or perpendicular to the samples surfaces. Figure 4.4 shows that corresponding features can be recognised, but shapes and sizes in both images are not completely the same. Additionally, the visual information

beyond the sample surface makes it difficult to directly link the SEM images to CT slices, as grain boundaries are far more difficult to detect in the SEM images. Landmarks were selected manually after visually looking for corresponding zones in the CT volume and SEM images (figure 4.4). Landmarks in the CT volume were spread across 50 to 100 slices, since sample surfaces were not perfectly parallel to the orientation of the slices. Since manual placement of landmarks creates an inevitable error, about 100 locations per surface were selected as registration landmark, to average out this error. This proved to be enough for a qualitative grain-to-grain match between different datasets. Registration was done in two steps: first a rigid rotation was performed to rotate the SEM images in the same planes of the surfaces of the volume, using only four landmarks in the corners of both the SEM image and the corresponding surface in the SEM volume. Afterwards, an X/Y translation step was performed, combined with image warping to compensate for the difference in feature form in both imaging methods.

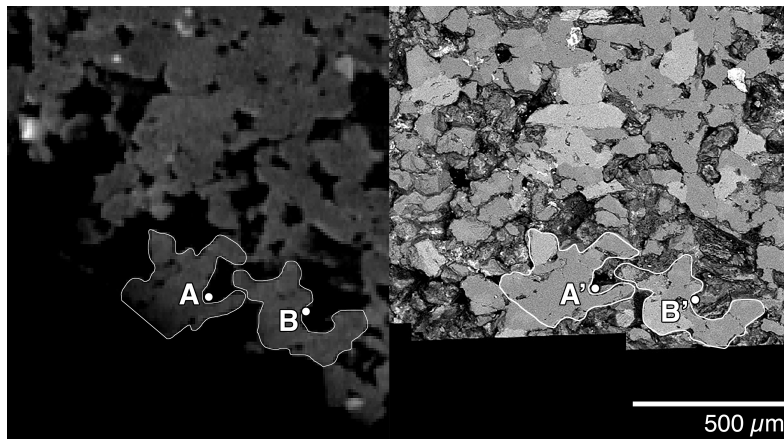


Figure 4.4: 2D to 3D image registration. White lines indicate corresponding areas in CT slice (left) and SEM image (right). White dots indicate possible points for landmark placement (A, A' and B, B').

3D-to-3D

The final type of image registration links the reconstructed microplug CT scan to the larger CT scan of the base sample (3D-to-3D registration). Since geological materials like the Vosges sandstone and other

construction materials such as concrete and bricks, are heterogeneous in nature, it is important to pinpoint the location of a sub-sample. If a sub-sample is very small (in this case, < 1 mm), the properties derived from this one microplug might not be representative for the entire sample. As in the 2D-to-3D registration step, semi-automatic landmark registration was performed to create the alignment between the small and large 3D volume and this time, rigid transformation was used to align the images. It should be stressed that the resolution in the lowest resolution CT scan was insufficient for direct selection of these landmarks. Even more, the 2D-to-3D registration of the SEM images to the low-resolution scan is an absolute must if one wants to know the exact location of the microplug in the large sample. Figure 4.5 shows that first, landmarks A and B were selected in the low-resolution tomogram and the SEM image. Finding landmark A in the high-resolution scan was much more easy, as spatial resolution and contrast are high enough in that volume. A combination of these points, together with some other points, made it possible to register the microplug into the cuboid.

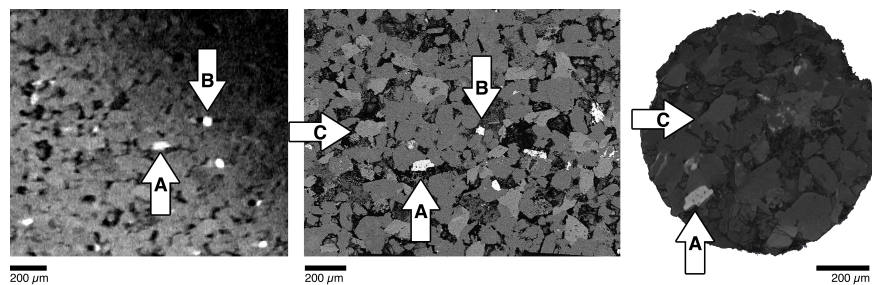


Figure 4.5: 3D-to-3D registration using landmarks. Left: Low-resolution CT; center: Registered SEM image; Right: High-resolution CT. The SEM image in the middle is used as an intermediary image to be able to find corresponding points.

Figure 4.6 shows the importance of this last image registration step. The small microplug is indicated in red inside the larger sample, which has been partially made transparent. High-density minerals are not distributed uniformly throughout the sample, and porosity is not the same throughout the entire sample. Indication of the location of the first subsample can help to set a strategy for further subsampling, or to determine which zones in the sample will have the same (flow) parameters as the microplug.

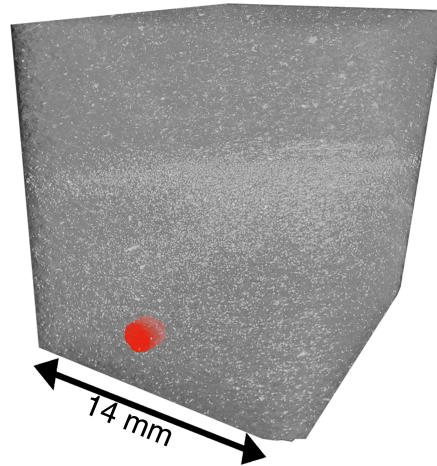


Figure 4.6: Location of the microplug (= 1 mm) in the full sample (width = 14 mm). The partially transparent full sample reveals that dense minerals, i.e. represented in lighter grey, are unevenly distributed throughout the material.

4.4.4 Focused ion beam nanotomography

Using FIB-nt, particular zones of interest could be selected and analysed at very high resolution in 3D. Figure 4.7 shows a BSE image of an area consisting of fine-grained minerals, which could not be resolved using μ CT. Using the FIB and electron beam, a $17 \times 17 \times 10 \mu\text{m}^3$ volume was imaged, with a voxel size of 34 nm. Due to the non-conductivity of the material, a lot of charging artifacts were present, and contrast was low. The images give a nice indication and view of the microstructure of the fine-grained micas and clay minerals; however, it was not possible to do any type of quantitative image analysis on them. The results are preliminary and the correct acquisition parameters should be found to enable decent analysis of these type of data.

4.5 Discussion

Location and orientation of different mineral zones inside a sample

SEM combined with EDS gives useful information about the presence of different mineral phases inside the investigated sample. Furthermore, the

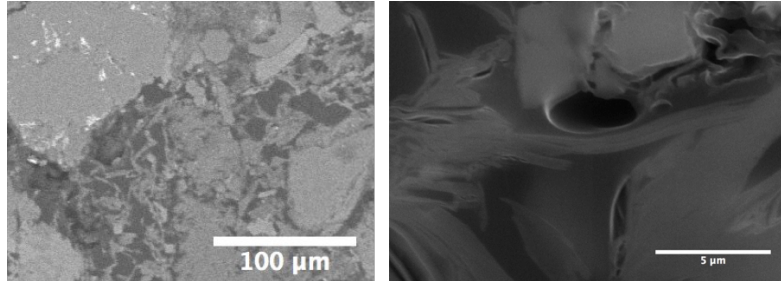


Figure 4.7: Left: BSE image of fine-grained area inside the Vosges sandstone; Right: FIB-nt slice of a similar area inside the stone. Different structures can clearly be observed, but not automatically quantified due to low contrast.

distribution of these phases in the 2D surfaces of the material is easily observed and analysed. When 2D mineral distribution maps are registered to the surfaces of a 3D volume, a pseudo-3D-look at the orientation and distribution of these minerals is obtained. This means that the iron-rich laminations can not only be observed, but also spatially oriented in the sample (figure 4.8, 3). This orientation can be compared to that of other features in the sample, and extrapolated to the samples interior.

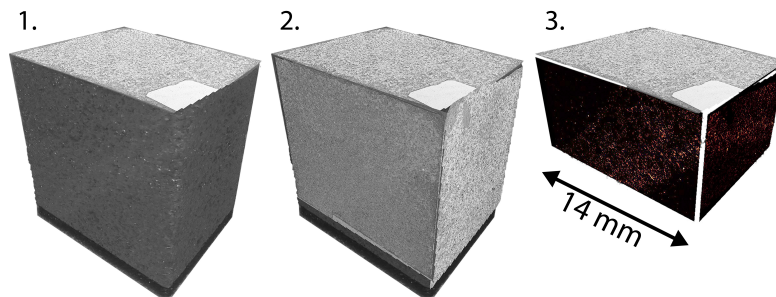


Figure 4.8: 1) Medium resolution CT volume with 1 SEM image registered to the top surface. 2) All SEM images registered to the surfaces of the CT volume. 3) EDS map for iron registered to two sides of the sample, showing the orientation of the observed iron oxide laminations.

Location of the sub-sample inside the base sample

Since geological materials like the Vosges sandstone are heterogeneous in nature, it is important to pinpoint the location of sub-samples in their parent sample. Zones with different structures or composition cannot always be identified in a macroscopic way, so verification of the sample

position has to be done through image registration. The medium resolution CT scan showed big regional differences in porosity and dense mineral content (figure 4.6), which means that it is important to know the location of the small subsample inside the big dataset. The scans at different resolutions reveal that multi-scale imaging is necessary to avoid inaccurate conclusions. Results illustrated that when the resolution gap between parent sample and sub-sample is too large, finding the location of the sub-sample in its parent is very hard to impossible, only based on the images. In this case additional information coming from SEM or other complementary techniques is a major aid, maybe even a necessity to make this 3D-to-3D image registration work. After localisation of the subsample, porosity of that area in the parent sample could be analysed and was found to be 11.3 %, of which about 2 % was closed porosity. Compared to the 9 % porosity of the overall sample, it is clear that the subsample was taken in a region with more than average porosity. However, 16 % can be interpreted as the correct porosity value, as the analysis error on the low-resolution data is just to high.

Higher-resolution imaging

Since standard μ CT cannot provide the resolution needed to resolve the finest features inside the Vosges stone, other methods should be addressed. In this study, first experiments using FIB-nt were performed, using secondary electron imaging. Results could be improved by combining serial sectioning with backscattered electron imaging. This will reduce charging of the sample, and additionally create a higher contrast between pores and grains. For applications where the sample is too important to destroy, FIB-nt is not an option. Other methods, e.g. high resolution μ CT at synchrotron facilities can provide images with resolutions below 100 nm (Kastner et al., 2010). In chapter 5, clay mineral and mica samples are imaged using ptychographic tomography (Dierolf et al., 2010) at the cSAXS beam line of the Paul Scherrer Institut in Villigen, Switzerland. Using this setup, resolutions of up to 16 nm in 3D have been reached (Holler et al., 2014).

4.6 Conclusions

At present, no image-based analysis technique can be considered as a multi-scale, all-area characterisation technique for heterogeneous porous

media. A combination of different imaging techniques, both 2D and 3D, followed by intensive post-processing of the acquired images can be used to provide more complete information on the analysed material. In the proposed methodology, medium-resolution μ CT results in three-dimensional, structural information of a large, centimetre-scale sample. Although the resolution is limited, large features can be identified, and interesting areas for further research are easily pinpointed. Data fusion of this medium-resolution 3D information with 2D imaging techniques such as SEM provide additional information in terms of structure. More importantly, the implementation of chemical analysis by means of EDS provides a pseudo-3D distribution of the different mineral phases present in the sample. Furthermore, SEM and EDS are mature and low-cost methods, accessible for most researchers in the field of materials characterisation. Sub-sampling the material allows for imaging at higher resolutions using lab-based CT, but the limit of this technique still lays at a spatial resolution of about 0.5 μ m. Since this is not enough to resolve the finest features inside the Vosges stone, other methods should be addressed. Therefore, other methods need to be implemented, such as FIB-nt, of which some preliminary results are shown in this paper. Synchrotron CT and ptychographic tomography (Dierolf et al., 2010) can be used for high-resolution imaging of fine-grained phases in natural stone. In all cases, coupling between different methods is a necessity, since the heterogeneity of natural materials causes the need for the exact localization of sub-samples in their parent sample. Image registration techniques in two or three dimensions have therefore become very important in image processing.

4.7 Acknowledgement

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References

- R.I. Al-Raoush and A. Papadopoulos. Representative elementary volume analysis of porous media using X-ray computed tomography. *Powder Technology*, 200(1-2):69–77, jun 2010. ISSN 00325910. doi: 10.1016/j.powtec.2010.02.011.
- Philipp Antrett. Characterization of an Upper Permian Tight Gas Reservoir. In *Springer Theses*, Springer Theses, pages 87–98. Springer Berlin Heidelberg, Berlin, Heidelberg, 2013. ISBN 978-3-642-36293-4. doi: 10.1007/978-3-642-36294-1. URL <http://link.springer.com/10.1007/978-3-642-36294-1>.
- P. Bésuelle, J. Desrues, and S. Raynaud. Experimental characterisation of the localisation phenomenon inside a Vosges sandstone in a triaxial cell. *International Journal of Rock Mechanics and Mining Sciences*, 37(8): 1223–1237, dec 2000. ISSN 13651609. doi: 10.1016/S1365-1609(00)00057-5.
- F.L. Bookstein. Size and shape spaces for landmark data in two dimensions. *Statistical Science*, 1(2):181–242, 1989.
- M Boone, J Dewanckele, V Cnudde, G Silversmit, E Van Ranst, P Jacobs, L Vincze, and L Van Hoorebeke. Three-dimensional phase separation and identification in granite. *Geosphere*, 7(1):79–86, 2011. doi: 10.1130/ges00562.1.
- M. A. Boone, P. Nielsen, T. De Kock, M. N. Boone, M. Quaghebeur, and V. Cnudde. Monitoring of stainless-steel slag carbonation using X-ray computed microtomography. *Environmental Science and Technology*, 48:674–680, 2014. ISSN 0013936X. doi: 10.1021/es402767q.
- L. Brabant, J. Vlassenbroeck, Y. De Witte, V. Cnudde, M. N. Boone, J. Dewanckele, and L. Van Hoorebeke. Three-Dimensional Analysis of High-Resolution X-Ray Computed Tomography Data with Morpho+.

- Microscopy and Microanalysis*, 17(2):252–263, 2011. doi: 10.1017/s1431927610094389.
- O. A. Cirpka, C. Leven, R. Schwede, K. Doro, P. Bastian, O. Ippisch, O. Klein, and A. Patzelt. Tomographic Methods in Hydrogeology. In Michael Weber and Ute Münch, editors, *Tomography of the Earths Crust: From Geophysical Sounding to Real-Time Monitoring SE - 9*, Advanced Technologies in Earth Sciences, pages 157–176. Springer International Publishing, 2014. ISBN 978-3-319-04204-6. doi: 10.1007/978-3-319-04205-3{_}9. URL http://dx.doi.org/10.1007/978-3-319-04205-3{_}9.
- V. Cnudde and M.N. Boone. High-resolution X-ray computed tomography in geosciences: A review of the current technology and applications. *Earth-Science Reviews*, 123(fufu):1–17, aug 2013. ISSN 00128252. doi: 10.1016/j.earscirev.2013.04.003.
- W. De Boever, H. Derluyn, D. Van Loo, L. Van Hoorebeke, and V. Cnudde. Data-fusion of high resolution X-ray CT, SEM and EDS for 3D and pseudo-3D chemical and structural characterization of sandstone. *Micron*, apr 2015. ISSN 09684328. doi: 10.1016/j.micron.2015.04.003.
- T. De Kock, M. A. Boone, J. Dewanckele, W. De Boever, M. N. Boone, G. De Schutter, and E. Lehmann. Monitoring frost susceptibility of limestone faces. In *12th International Congress on the Deterioration and Conservation of Stone*, 2013.
- H. Derluyn, M. Griffa, D. Mannes, I. Jerjen, J. Dewanckele, P. Vontobel, a. Sheppard, D. Derome, V. Cnudde, E. Lehmann, and J. Carmeliet. Characterizing saline uptake and salt distributions in porous limestone with neutron radiography and X-ray micro-tomography. *Journal of Building Physics*, 36(4):353–374, jan 2013. ISSN 1744-2591. doi: 10.1177/1744259112473947.
- J. Dewanckele, T. De Kock, G. Fronteau, H. Derluyn, P. Vontobel, M. Dierick, L. Van Hoorebeke, P. Jacobs, and V. Cnudde. Neutron radiography and X-ray computed tomography for quantifying weathering and water uptake processes inside porous limestone used as building material. *Materials Characterization*, 88:86–99, feb 2014. ISSN 10445803. doi: 10.1016/j.matchar.2013.12.007.
- M. Dierolf, A. Menzel, P. Thibault, P. Schneider, C. M. Kewish, R. Wepf, O. Bunk, and Franz Pfeiffer. Ptychographic X-ray computed tomography

- at the nanoscale. *Nature*, 467(7314):436–9, sep 2010. ISSN 1476-4687. doi: 10.1038/nature09419.
- M. Holler, A. Diaz, M. Guizar-Sicairos, P. Karvinen, E. Färm, E. Härkönen, M. Ritala, A. Menzel, J. Raabe, and O. Bunk. X-ray ptychographic computed tomography at 16 nm isotropic 3D resolution. *Scientific reports*, 4:3857, jan 2014. ISSN 2045-2322. doi: 10.1038/srep03857.
- L. Holzer, F. Indutnyi, P. H. Gasser, B. Münch, and M. Wegmann. Three-dimensional analysis of porous BaTiO₃ ceramics using FIB nanotomography. *Journal of microscopy*, 216(Pt 1):84–95, oct 2004. ISSN 0022-2720. doi: 10.1111/j.0022-2720.2004.01397.x.
- Lorenz Holzer and Marco Cantoni. REVIEW OF FIB TOMOGRAPHY. In UTKE, editor, *Nanofabrication Using Focused Ion and Electron Beams*, pages 410–435. 2011.
- C. R. Huddleston-Holmes and R. A. Ketcham. Getting the inside story: Using computed X-ray tomography to study inclusion trails in garnet porphyroblasts. *American Mineralogist*, 90:1918, 2005. ISSN 0003004X. doi: 10.2138/am.2005.1840.
- K. Jiao, S. Yao, C. Liu, Y. Gao, H. Wu, M. Li, and Z. Tang. The characterization and quantitative analysis of nanopores in unconventional gas reservoirs utilizing FESEMFIB and image processing: An example from the lower Silurian Longmaxi Shale, upper Yangtze region, China. *International Journal of Coal Geology*, 128-129: 1–11, aug 2014. ISSN 01665162. doi: 10.1016/j.coal.2014.03.004.
- E. I. Jussiani and C. R. Appoloni. Effective atomic number and density determination of rocks by X-ray microtomography. *Micron (Oxford, England : 1993)*, 70C:1–6, nov 2014. ISSN 1878-4291. doi: 10.1016/j.micron.2014.11.005.
- J. Kastner, B. Harrer, G. Requena, and O. Brunke. A comparative study of high resolution cone beam X-ray tomography and synchrotron tomography applied to Fe- and Al-alloys. *NDT & E international : independent nondestructive testing and evaluation*, 43(7-3):599–605, oct 2010. ISSN 0963-8695. doi: 10.1016/j.ndteint.2010.06.004.
- Lukas M. Keller, Lorenz Holzer, Roger Wepf, Philippe Gasser, Beat Münch, and Paul Marschall. On the application of focused ion beam nanotomography in characterizing the 3D pore space geometry of

- Opalinus clay. *Physics and Chemistry of the Earth, Parts A/B/C*, 36(17-18):1539–1544, jan 2011. ISSN 14747065. doi: 10.1016/j.pce.2011.07.010.
- R. A. Ketcham and W. D. Carlson. Acquisition, optimization and interpretation of X-ray computed tomographic imagery: applications to the geosciences. *Computers & Geosciences*, 27(4):381–400, 2001.
- D. Lagrou, R. Dreesen, and L. Broothaers. Comparative quantitative petrographical analysis of Cenozoic aquifer sands in Flanders (N Belgium): overall trends and quality assessment. *Materials Characterization*, 53(2-4):317–326, nov 2004. ISSN 10445803. doi: 10.1016/j.matchar.2004.07.012.
- B. Masschaele, M. Dierick, D. Van Loo, M. N. Boone, L. Brabant, E. Pauwels, Veerle Cnudde, and Luc Van Hoorebeke. HECTOR: A 240kV micro-CT setup optimized for research. *Journal of Physics: Conference Series*, 463:012012, oct 2013. ISSN 1742-6596. doi: 10.1088/1742-6596/463/1/012012.
- N. Matsuoka and J. Murton. Frost weathering: Recent advances and future directions. *Permafrost and Periglacial Processes*, 19(2):195–210, 2008. doi: 10.1002/ppp.620.
- T G Nijland, C W Dubelaar, T J Wijffels, and T J M van der Linden. Zwartverkleuring van Bentheimer, Obernkirchener en Rakowicze zandsteen. *Praktijkreeks Instandhouding Monumenten*, Deel II-4, 2004.
- S.J.B. Reed. *Electron Microprobe Analysis and Scanning Electron Microscopy in Geology*. Cambridge University Press, 2005. ISBN 9780521848756. doi: <http://dx.doi.org/10.1017/CBO9780511610561>.
- R. M. Sok, T. Varslot, A. Ghous, S. Latham, A. P. Sheppard, and M. A. Knackstedt. Pore Scale Characterization of Carbonates at Multiple Scales: Integration of Micro-CT, BSEM, and FIBSEM. *Petrophysics*, 51(6):379–387, 2010.
- J. Vlassenbroeck, M. Dierick, B. Masschaele, V. Cnudde, L. Hoorebeke, and P. Jacobs. Software tools for quantification of X-ray microtomography. *Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment*, 580(1):442–445, 2007. doi: 10.1016/j.nima.2007.05.073.
- D. Wildenschild and A. P. Sheppard. X-ray imaging and analysis

techniques for quantifying pore-scale structure and processes in subsurface porous medium systems. *Advances in Water Resources*, 51 (0):217–246, 2013. ISSN 0309-1708. doi: <http://dx.doi.org/10.1016/j.advwatres.2012.07.018>.

5

Structural and chemical characterisation of clay minerals in sandstone using ptychographic tomography

In this chapter, ptychographic tomography is used for 3D imaging of fine-grained minerals at very high resolutions. This chapter is based on a paper that has been published in *Applied Clay Science* as *Characterization of composition and structure of clay minerals in sandstone with ptychographic X-ray nanotomography*. - **Wesley De Boever**, Ana Diaz, Hannelore Derluyn, Jeroen Van Stappen, Tim De Kock, Jan Dewanckele, Tom Bultreys, Matthieu Boone, Thomas De Schryver, Eirik T. B. Skjønsgjell, , Mirko Holler, Dag W. Breiby, Veerle Cnudde. The Ph.D. candidate was responsible for the experiments, sample preparation and analyses. Ana Diaz was the beam line scientist during cSAXS experiments and had a large input in the technical description of the setup and method. Dag Breiby and Eirik Skjønsgjell supplied the relative humidity setup described in this chapter. All other co-authors assisted the first author during the experimental campaigns at the PSI.

Changes in porosity and pore morphology inside clay minerals or other phyllosilicates such as micas, present in small amounts inside sandstones, have a great influence on the permeability and strength of natural stone, which is extremely important for the durability of building stones. It has been long suggested that even non-swelling clay laminations in stones can act as preferential paths for capillary absorption (Winkler, 1968), causing them to be weak zones vulnerable to frost damage or even non-freezing thermal cycling (Cnudde et al., 2013; Winkler, 1968). The presence of clay minerals inside stones can cause their expansion at higher relative humidity, having an effect on the materials mechanical properties (Van Den Abeele et al., 2002). Damage is further extended when swelling clays are present, creating substantial damage to buildings and monuments (Gutiérrez et al., 2012; Sebastián et al., 2008; Wangler et al., 2011; Wangler and Scherer, 2008). Although the importance of clay minerals inside (building) stones is known, up to now no methods were available to visualize their behavior under different external conditions on the pore scale. Non-destructive 3D characterisation of geological materials at μm scale resolution has been made possible by the rapid development of high-resolution X-ray tomography (μCT) over the last few decades (Ketcham and Carlson, 2001; Cnudde and Boone, 2013; Wildenschild and Sheppard, 2013). The use of μCT has enabled the extraction of the pore morphology and pore network models directly from 3D images of a raw material. However, traditional lab-based μCT lacks the spatial resolution to obtain information about pores and grains in the size range below $1\text{ }\mu\text{m}$. Although current laboratory setups using optics can reach nominal resolutions as low as 50 nm , these systems typically operate at low energies, have very long scan times and cannot provide the flexibility to attach large peripheral equipment for the conditioning of samples. Porosity in tight materials such as shales or mudstones has traditionally been characterised by scanning electron microscopy (SEM), combined with extrapolation of 2D images to 3D space, for example by process-based modelling (Øren and Bakke, 2002). Later, the use of a focused ion beam (FIB) combined with SEM, called FIB-nanotomography (FIB-nt) enabled direct 3D imaging of samples, at spatial resolutions comparable to traditional SEM images, i.e. down to several tens of nanometer in 3D (Holzer et al., 2004; Keller, 1978). Unfortunately, neither of those techniques are non-destructive or allow for in situ conditioning and monitoring of the samples. Currently, non-destructive 3D imaging at high resolution is typically done using μCT at synchrotron beam lines,

where resolutions just below 100 nm can be reached (Baruchel et al., 2006), which is still not enough for quantitative analysis of the clay mineral fraction inside a sandstone.

In this chapter, quantitative imaging of nano-scale structures and composition of clay mineral clusters from different types of sandstone at different levels of relative humidity was performed at resolutions that until now could only be achieved by FIB-nt in an intrinsically destructive manner (Keller et al., 2013). In previous X-ray imaging studies of the swelling behaviour of clays (Harjupatana et al., 2015; Tomioka et al., 2010), the obtained resolution was not high enough, and the average behaviour of an entire, larger sample was analysed. Even X-ray tomography at very high resolutions and small (0.8 mm) samples cannot resolve individual pores (Suuronen et al., 2014), although these approaches provide valuable information about the orientation of swelling and shrinking processes in clay minerals. The open and flexible configuration of our experimental setup allows for the positioning of peripheral equipment for conditioning of the samples environment during measurements. This enabled to gain 3D insights on the nanometer scale inside clay minerals while adapting to the relative humidity. The relative humidity of the samples environment during measurements at the beam line was controlled using the same conditioning setup as for a recently reported study on the hydration behaviour of silk fibers (Esmaeili et al., 2013). The non-destructive nature of ptychographic imaging allows for a comparison of the morphology of the analysed samples under dry (5 % R.H.) and wet (95 % R.H.) conditions, thus studying the influence of relative humidity on the 3D structure and the dynamics of clay minerals that are present inside sandstones.

5.1 Materials

Fine-grained minerals were extracted from both the Vosges sandstone and Kandla grey sandstone, since these types of minerals are present in both stones, and we know that these fine-grained minerals have an effect on the petrophysical behaviour of the stone.

5.2 Methods

5.2.1 Sampling

From both stones, several samples were taken for various types of experiments. For the first set of experiments, samples of approximately 50 μm in diameter were selected, corresponding to samples V1 and V2 for the Vosges sandstone and K1 for Kandla Grey. For a follow-up experiment using a different setup, a 25 μm Vosges sandstone sample, V3, was prepared. First, preparation of the samples using a focused ion beam, following the method of Lombardo et al. (2012) was attempted, but the required sample size proved to be too large to prepare samples in a reasonable time, and the material was too complicated for this procedure. Therefore, all samples were handpicked under a binocular microscope, from a bulk of scraped-off material. Using a needle, samples were positioned on a special sample mount for the nanopositioning instrument (Holler et al., 2014), and secured in place using UV-hardening glue. For the smaller V3 sample, the adhesive of standard tape was used to attach the samples. Since this sampling procedure involves scraping and grinding of the material, the structure of the samples might have changed during this procedure. However, we expect this effect to be minimal, as the samples proved to be intact and solid after analysis.

5.2.2 Ptychographic tomography

Ptychographic experiments were carried out at the cSAXS beam line (X12SA) of the Swiss Light Source at the Paul Scherrer Institute in Villigen, Switzerland (figure 5.1). The first set of measurements was performed on samples V1, V2 and K1 using a beam energy of 7 keV and a modular setup including a piezoelectric-driven stage on top of a rotation stage, as described by Dierolf et al. (2010). A Fresnel zone plate made of Au (Gorelick et al., 2011) with 150 μm diameter, 90 nm outer-most zone width, and 76.2 mm focal length was used to define a coherent illumination with a flux of about 4×10^8 photons/s. The sample was placed at 4.0 mm downstream of the focus, where the beam had a size of about 8 μm . The sample was scanned in a non-periodic grid following the pattern of a Fermat spiral, as described in (Huang et al., 2014), with an average step size of 2.5 μm , ensuring enough overlapping of the illumination at

consecutive scanning positions. We estimate a flux density of about 6×10^6 photons/ μm^2 during these scans. At each scanning position, coherent diffraction patterns with 0.1 s acquisition time were recorded with an Eiger 500k detector with a pixel size of 75 μm (Dinapoli et al., 2011) placed 7.223 m downstream of the sample with a He-filled flight tube in between to reduce parasitic scattering and absorption. The field of view of the scans varied for each sample, being $40 \times 20 \mu\text{m}^2$ (horizontal x vertical) for sample V1, $50 \times 20 \mu\text{m}^2$ for V2 and $60 \times 20 \mu\text{m}^2$ for K1. Ptychographic scans were repeated at different angular positions of the sample with respect to the incoming beam ranging from 0 to 180 degrees in equal angular steps, comprising a total of 320 angular projections for specimen V1 and 480 for specimens V2 and K1. The total time for a full tomographic measurement took from 8 to 13 hours, depending on the specimens volume. The total dose imparted during each tomographic scan was estimated as described in (Howells et al., 2009) to be about 1×10^7 Gy for samples V1 and V2, assuming that they are mostly composed of Goethite, and about 2×10^7 Gy for sample K1, assuming it is mostly composed of muscovite. During these experiments, samples were conditioned at two relative humidity values, namely a dry state at about 5 % R.H. and a humid state at about 95 % R.H.. Relative humidity was controlled by placing a cylinder-shaped polymer cap equipped with an X-ray transparent Si_3N_4 window over the sample, as described in Esmaeili et al. (2013). A constant flow of dry N_2 was maintained inside that cup to impose the dry state. This conditioning was done directly on the setup, ensuring that the conditions did not change during the measurements. Samples were placed in the path of the X-ray beam and conditioned for half an hour before starting the measurement. After the dry measurement the flow of N_2 was humidified by bubbling the gas through water (Esmaeili et al., 2013). The wet measurement was started after one hour of conditioning the sample. A relative humidity sensor was placed next to the sample inside the environmental cap and humidity values were monitored and logged at all times during the measurements. For each projection, ptychographic reconstructions were done online using a region of 500×500 pixels of the detector, using an algorithm based on the difference map (Thibault et al., 2009) followed by a maximum likelihood refinement (Thibault and Guizar-Sicairos, 2012). The pixel of the reconstructed images had a size of 34 nm. A second experiment was performed for sample V3 with the setup described by Holler et al. (2014), which uses laser interferometry for accurate positioning of the sample with respect to

the beam-defining optics. Due to the characteristics of this setup, conditioning of the samples during measurements is not possible, and all experiments were performed at ambient temperature of about 24° C and relative humidity of about 40 %. However, the increased stability of this setup allowed for higher resolution imaging. The experiment was done at 6.2 keV photon energy, using a similar FZP with 170 μm diameter and 60 nm outer-most zone width, which has a focal length of 51.0 mm at this energy, providing a flux of 7×10^8 photons/s. The sample was placed 0.9 mm downstream the focus, in such a way that the illumination had a size of 3 μm at the sample position. Ptychographic scans were performed following a Fernal spiral pattern with a field of view of $30 \times 16 \mu\text{m}^2$ (horizontal x vertical) with an average spacing between consecutive points of about 1.2 μm , providing a flux density of about 5×10^7 photons/ μm^2 . Coherent diffractions patterns of 0.1 s exposure time were recorded at each scanning positions with a Pilatus 2M detector with 172 μm pixel size (Kraft et al., 2009) placed 7.346 m downstream of the sample. These scans were repeated for a total of 800 angular projections, imparting a total estimated dose of 2×10^8 Gy on the specimen over a time of about 24 hours. The dose estimation was done assuming that the sample is mostly composed of goethite. Because in this case diffraction patterns extended over areas larger than the size of a single detector module, we acquired angular projections at alternating detector positions (Holler et al., 2014) to constrain the ptychographic reconstructions in areas of the detector where no data is measured due to intermodule gaps. Ptychographic reconstructions were then carried out with data sets at two different detector positions simultaneously, enforcing the illumination to be the same, using the algorithm described in (Guizar-Sicairos et al., 2014), which uses the same ptychographic reconstruction algorithms mentioned earlier. Using 500×500 pixels of the detector resulted in reconstructed images with a pixel size of 17 nm. For all experiments, the post processing of the reconstructed projections consisted of removal of zeroth and first-order phase terms, phase unwrapping, projection alignment and tomographic reconstructions, as described in (Guizar-Sicairos et al., 2011). An additional alignment of the projections in the horizontal direction based on tomographic consistency was done (Guizar-Sicairos et al., 2015). Analysis of the obtained images was performed by using a combination of Octopus Analysis (Brabant et al. (2011) ; www.insidematters.eu), Fiji (Schindelin et al. (2012); www.fiji.sc), and Avizo (www.fei.com). For comparison between dry and wet measurements, samples were registered

to compensate for minimal movements of the sample using rigid registration modules in Avizo. For chemical analysis, the peaks in the histograms of the datasets were analysed to determine the electron density of the different phases inside the sample. The standard deviation of the distribution was used to determine the spread on the measurement. We show electron density maps of the specimens and identify different minerals based on their estimated mass densities.

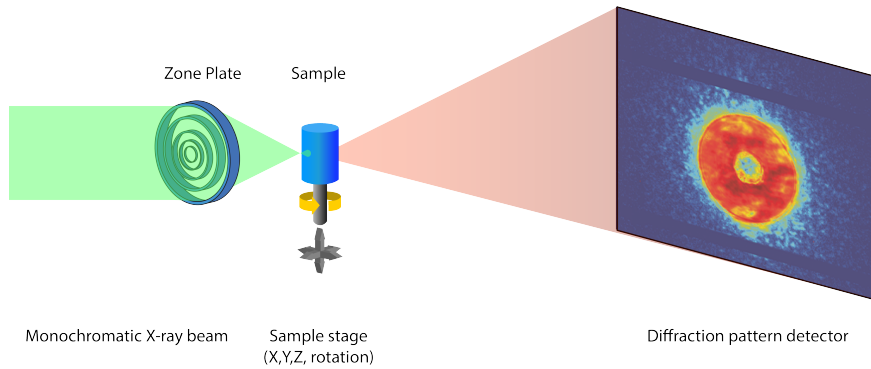


Figure 5.1: Schematic representation of the experimental setup. A monochromatic, coherent X-ray beam is focused using a Fresnel zone plate and the specimen is placed a few millimetre after the focus. The sample is mounted on a translation stage that allows horizontal, vertical and rotational movement. Diffraction patterns are detected in the far field with a 2D detector placed about 7.2 m downstream of the sample.

5.3 Results and discussion

5.3.1 Vosges sandstone

Three Vosges sandstone samples were analysed: two during the first experimental sequence (V1 and V2) at a spatial resolution of 88 and 106 nm, and a third sample (V3) at the high-resolution setup, obtaining a spatial resolution of 45 nm. The spatial resolution was determined by Fourier shell correlation from two independent tomograms, each of them reconstructed from half the number of projections, as described in (Holler et al., 2014), and using the half-bit threshold criterion (van Heel and Schatz, 2005). During measurements of both V1 and V2, the relative

humidity was controlled; however, sample preparation was very challenging for these sample sizes, and V2 got contaminated with UV-hardening glue, making it impossible to observe changes due to R.H. variations. Consequently, only sample V1 could be used for wet vs. dry comparison. Despite the contamination, sample V2 provided valuable information about morphology of its pore system and composition. Sample V1 is composed of one single material, being a large grain with some very fine laminations at the sides of the sample. The sample showed expansion of the finest lamina in the clay minerals and an overall decrease of porosity inside the sample due to swelling of the clays at high R. H. As was to be expected, changes were subtle, but still significant. Figure 5.2 shows a detail from the histogram of both volumes, zoomed in to the grey value range representing the material. In this range, a small increase of about 1.3 % in volume from dry to wet state can be detected. Both samples were analyzed using the same procedure in order to be able to compare results. Close comparison of the dry and humid images shows a slight decrease in porosity, especially in the smallest pores, at the very limit of the resolution (figure 5.3). Results have to be interpreted with care, since these changes are very small, but it can be stated that the method is capable of tracking subtle structural 3D changes. Moreover, the sample did not consist of typically swelling clays such as smectites, explaining why changes are so minimal.

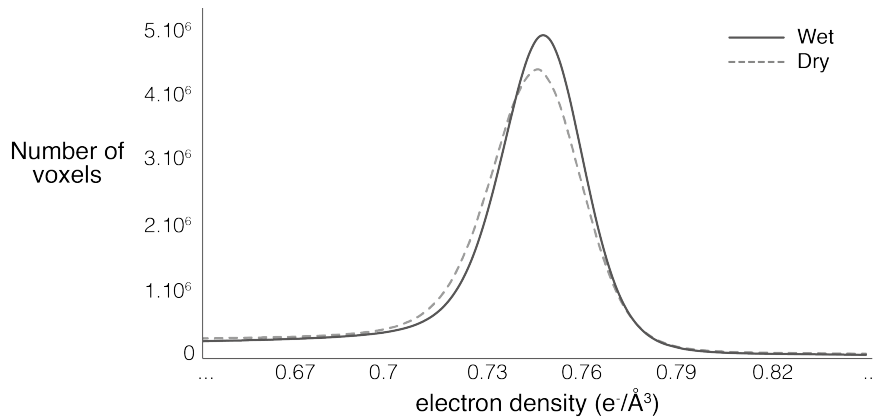


Figure 5.2: Comparison of a part of the histogram of the wet and dry volume of sample V1. The height of the peak, corresponding to solid material and located at an 8 bit grey value of about 145, slightly increases from the dry to wet state. This is caused by slight swelling of the material.

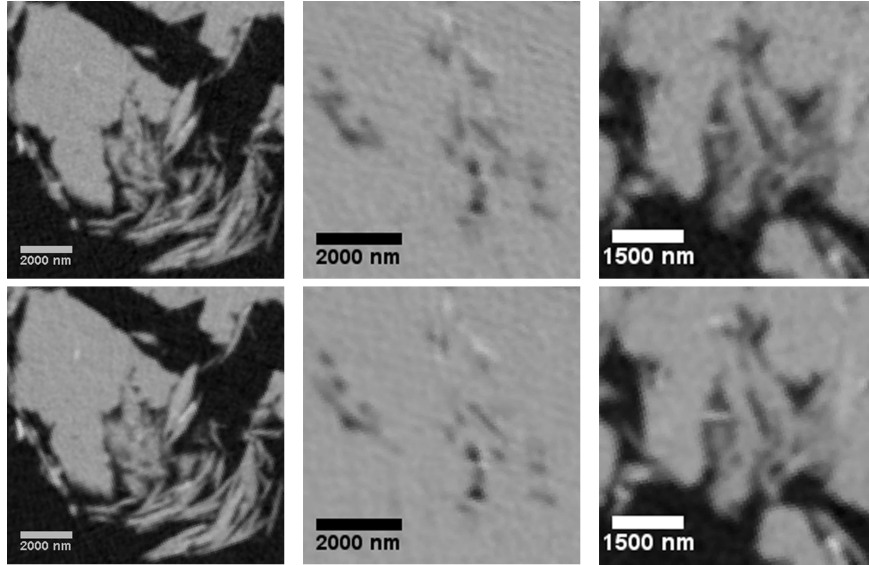


Figure 5.3: Comparison between dry (top) and humid (bottom) images of V1. Overall a small decrease in porosity is visible due to swelling of the material.

Sample V2 is completely surrounded by a drop of glue, but shows clear contrast in different densities (figure 5.4). The histogram of the dataset reveals four peaks, as shown in figure 5.5: the first one being at electron density = 0, representing the air (N_2 gas) around the sample. The second peak lies at electron density $(0.417 \pm 0.042) \text{ e}^-/\text{\AA}^3$, and corresponds to the glue surrounding the sample. The two peaks at the highest values are the mineral phases at $(0.701 \pm 0.066) \text{ e}^-/\text{\AA}^3$ and $(1.08 \pm 0.03) \text{ e}^-/\text{\AA}^3$ corresponding to smectite clay minerals, from which montmorillonite $((Na,Ca)_{0.3}(Al,Mg)_2(Si_4O_{10})(OH)_2.nH_2O)$ gave the best match and goethite (FeO_2H) respectively. The A/Z ratio of montmorillonite of 2.001 g/mol was used for the conversion to mass density, subsequently of the smectite is found to be $(2.33 \pm 0.22) \text{ g/cm}^3$. For comparison, the theoretical average is 2.35 g/cm^3 . For goethite we measured a value of $(3.70 \pm 0.12) \text{ g/cm}^3$, while its theoretical average value is 3.8 g/cm^3 .

The images of the scanned V3 sample provided very valuable information concerning the mineralogical composition and structure of the Vosges sandstone. V3 consisted of one big grain of mica (muscovite), which is partly lined with iron oxide particles, most likely to be hematite, which appears as the densest phase in the images (figure 5.6). These hematite

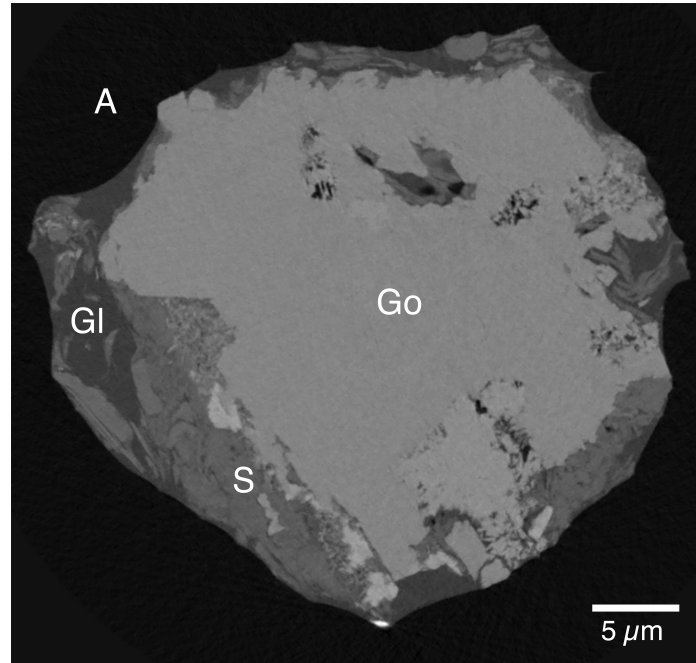


Figure 5.4: Tomographic slice of sample VI. Go = goethite; S = smectite; Gl = glue and A = air.

particles cause the red to pink macroscopic color of the Vosges sandstone. This phase was segmented by thresholding with Octopus Analysis (Brabant et al., 2011), and the individual particles were analysed. Analysis of the minimum closing distance, defined as the diameter of the smallest sphere that can completely surround a particle, revealed that the main portion of these particles was around 200 nm in diameter, with only 66 out of about 14000 particles being bigger than 1 μm (figure 5.7). This means that these particles could not be observed in 3D by most imaging techniques, including μCT , and are even too small to be observed using light microscopy. Furthermore, the weak attachment of these iron oxides to larger grains means that they have a high likelihood of being washed or polished out during sample preparation for FIB-SEM measurements.

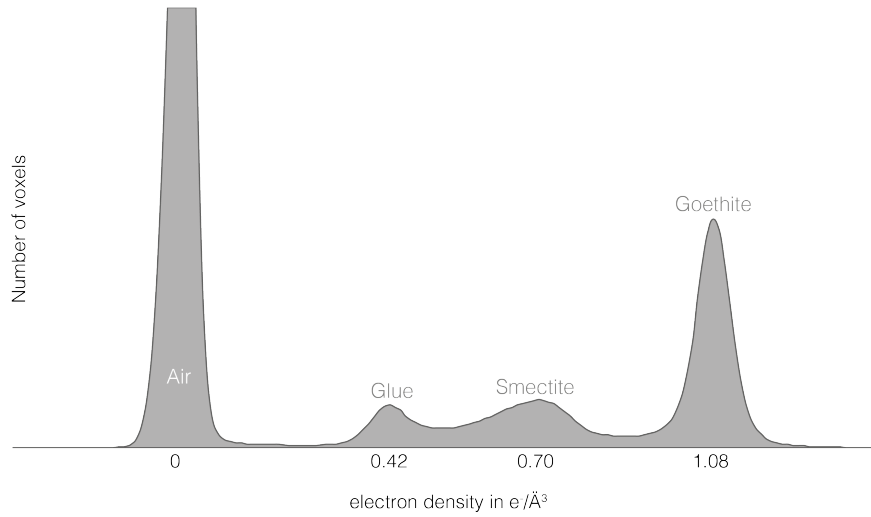


Figure 5.5: Histogram of dataset corresponding to sample V2. The histogram reveals four different peaks, corresponding to the air surrounding the sample, the UV glue, smectite minerals and goethite. The air peak has been cut off for representation purposes.

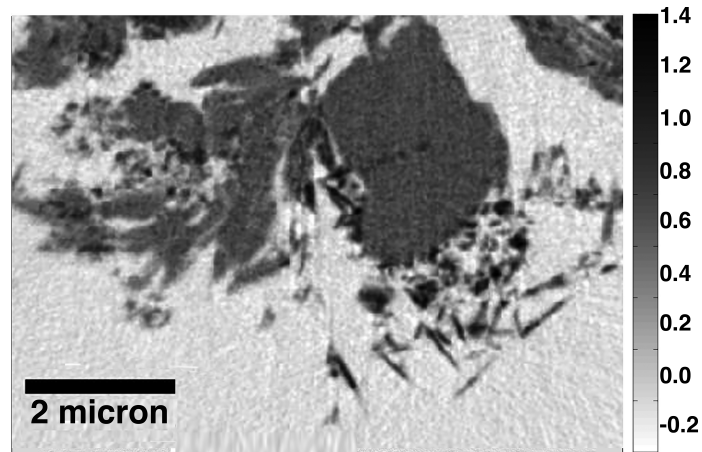


Figure 5.6: Detail of V3 tomogram. Grey values represent electron density in $e/\text{\AA}^3$. The densest (darkest) particles which probably correspond to iron oxide particles coating the grains. Intermediate grey values are the larger mica grain and light gray represents the air surrounding the sample.

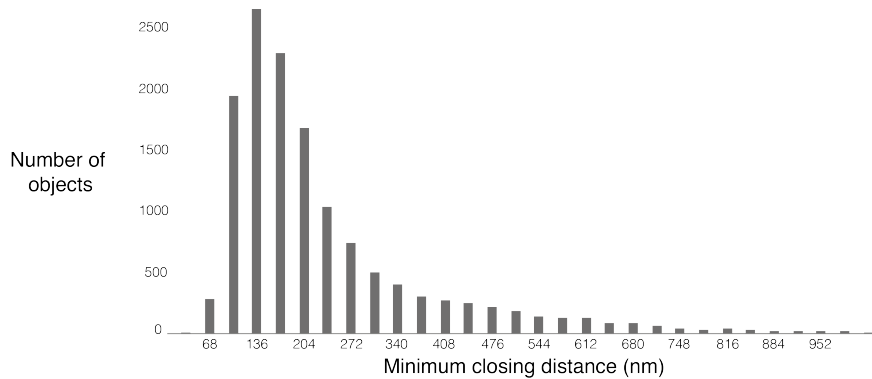


Figure 5.7: Size distribution of iron oxide particles in V3, based on minimum closing distance.

5.3.2 Kandla Grey

From the analysis of sample K1, a very good insight in the pore structure inside a cluster of fine-grained minerals was obtained. The observed plate shaped crystals and parallel cleavage of the material, as shown in figure 8, suggest that this is a mica mineral, and the electron density value (0.86 ± 0.12) $e^-/\text{\AA}^3$ corresponds to that of muscovite with a mass density of (2.86 ± 0.39) g/cm^3 . For comparison, the expected mass density of muscovite ranges from 2.77 to 2.88 g/cm^3 , with an average value of 2.83 g/cm^3 (source: www.webmineral.com). The images show clear contrast between solid material and pores, as well as a third phase. From the various menisci (figure 5.8) that can be observed, we must conclude that this phase originated from a liquid, and can be the solidified UV glue. This is confirmed by the fact that the electron density value of $0.414 e^-/\text{\AA}^3$ measured for this phase is the same as for the bubble that surrounds sample V2 (figure 5.4). Since the glue must have entered the sample during sample preparation, we can also classify this phase as being part of the porosity.

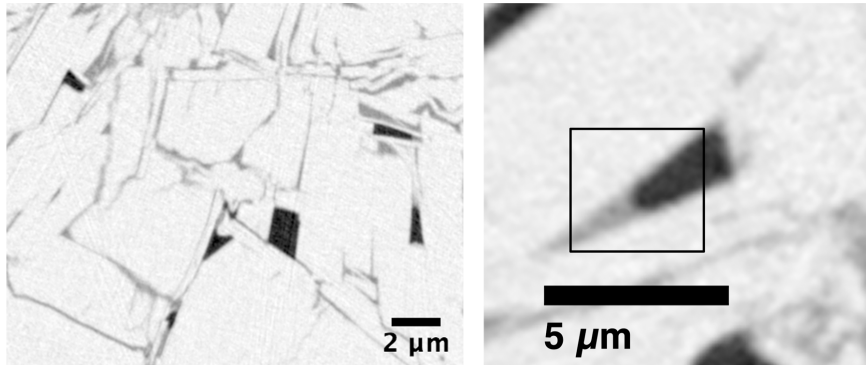


Figure 5.8: Details of sample K1. Left: the images show very good contrast between pores (black), solid (white) and a phase of intermediate density. Right: Transition between pores and intermediate phase has the shape of a meniscus, confirming this intermediate phase is a liquid.

The overall porosity, including glue-filled pores, of sample K1 was measured to be about 21 %, with all pores connected to each other. An indication of the width of the glue-filled, connecting pores was provided by measuring the maximum opening (Brabant et al, 2011) of these pores after segmenting them. The mean width was measured to be 234 ± 168

nm. The massive absorption of liquid in these very narrow pores, provides an explanation to why these muscovite layers are weak zones inside the Kandla Grey sandstone, causing the material to crack due to frost action (Cnudde et al., 2013).

5.4 Conclusions

Using ptychographic tomography, we imaged the most fine-grained fraction inside two sandstones at very high resolutions with excellent signal-to-noise ratio. As a non-destructive technique, X-ray ptychographic tomography enabled dynamic experiments, visualising the effect of relative humidity on the imaged clay minerals. Although these effects have been measured on a macroscopic scale (Van Den Abeele et al., 2002), the precise effects on the pore-scale level have never been visualised. We detected a measurable increase in volume and in density in the Vosges sample, as evidenced by the height increase and slight shift of the histogram peak corresponding to the clay material. This is important, since even slight expansion of interlayer water can cause material fatigue, eventually leading to failure (Winkler, 1968). The same methodology can be used for other materials that are more susceptible to changes in relative humidity such as smectites, where swelling of clays can create large damage (Gutiérrez et al., 2012; Sebastián et al., 2008; Wangler et al., 2011). In future experiments, it should be possible to visualise the water inside clay minerals, as the electron density value of water is $0.33 \text{ e}^-/\text{\AA}^3$, and therefore certainly detectable by ptychographic tomography. In order for this to succeed, a more sophisticated method for sample preparation and fixation should be developed, as the required samples are too large to be milled out using FIB in a realistic time-frame, and manual attachment is not precise enough. Analysis of the Kandla Grey sample confirmed that mica laminations, although not swelling, can create weak spots in a sandstone (Cnudde et al., 2013), due to their preferential absorption paths for liquids. When exposed to water, water gets absorbed into the fine pore network of these mica laminations, where it has no room to expand when it freezes. A big advantage of the method is the extraction of quantitative information on refractive index, electron density and mass density, enabling the identification of the minerals that are present. Results using a high-resolution setup showed the distribution of sub-micrometer iron oxide particles coating the grains of the sandstone, and giving it its

distinctive pink colour. Distribution of smectite and goethite inside the clay fraction of the Vosges sandstone was visualised and these two minerals were identified without prior knowledge of sample composition. Although most of the results and their interpretation have been formulated from a building stone perspective, the methodology introduced here may prove interesting for the geoscience community as a whole. The visualisation and quantification for the characterisation of the pore system inside clay mineral clusters can provide important results for fluid flow modelling, where sub-resolution porosity in computed tomography data is often a problem for exact results (Bultreys et al., 2015), and can have important applications in research on shale reservoirs, nuclear waste storage and other fields where non-destructive imaging can be an advantage.

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References

- J. Baruchel, J-Y. Buffiere, P. Cloetens, M. Di Michiel, E. Ferrie, W. Ludwig, E. Maire, and L. Salvo. Advances in synchrotron radiation microtomography. *Scripta Materialia*, 55(1):41–46, jul 2006. ISSN 13596462. doi: 10.1016/j.scriptamat.2006.02.012.
- L. Brabant, J. Vlassenbroeck, Y. De Witte, V. Cnudde, M. N. Boone, J. Dewanckele, and L. Van Hoorebeke. Three-Dimensional Analysis of High-Resolution X-Ray Computed Tomography Data with Morpho+. *Microscopy and Microanalysis*, 17(2):252–263, 2011. doi: 10.1017/s1431927610094389.
- T. Bultreys, L. Van Hoorebeke, and V. Cnudde. Multi-scale, micro-computed tomography-based pore network models to simulate drainage in heterogeneous rocks. *Advances in Water Resources*, 78:36–49, apr 2015. ISSN 03091708. doi: 10.1016/j.advwatres.2015.02.003.
- V. Cnudde and M.N. Boone. High-resolution X-ray computed tomography in geosciences: A review of the current technology and applications. *Earth-Science Reviews*, 123:1–17, aug 2013. ISSN 00128252. doi: 10.1016/j.earscirev.2013.04.003.
- V. Cnudde, W. De Boever, J. Dewanckele, T. De Kock, M. Boone, M.N. Boone, G Silversmit, L. Vincze, E Van Ranst, H Derluyn, S Peetermans, J Hovind, P Modregger, M Stampanoni, K De Buysser, and G De Schutter. Multi-disciplinary characterization and monitoring of sandstone (Kandla Grey) under different external conditions. *Quarterly Journal of engineering Geology and Hydrogeology*, 46:95–106, 2013. doi: 10.1144/qjegh2012-005.
- M. Dierolf, A. Menzel, P. Thibault, P. Schneider, C. M. Kewish, R. Wepf, O. Bunk, and Franz Pfeiffer. Ptychographic X-ray computed tomography at the nanoscale. *Nature*, 467(7314):436–9, sep 2010. ISSN 1476-4687. doi: 10.1038/nature09419.

- R. Dinapoli, A. Bergamaschi, B. Henrich, R. Horisberger, I. Johnson, A. Mozzanica, E. Schmid, Bernd Schmitt, Akos Schreiber, Xintian Shi, and Gerd Theidel. EIGER: Next generation single photon counting detector for X-ray applications. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 650(1):79–83, sep 2011. ISSN 01689002. doi: 10.1016/j.nima.2010.12.005.
- M. Esmaeili, J. B. Fløystad, A. Diaz, K. Høydalsvik, M. Guizar-Sicairos, J. W. Andreasen, and D. W. Breiby. Ptychographic X-ray Tomography of Silk Fiber Hydration. *Macromolecules*, 46(2):434–439, jan 2013. ISSN 0024-9297. doi: 10.1021/ma3021163.
- Sergey Gorelick, Joan Vila-Comamala, Vitaliy a. Guzenko, Ray Barrett, Murielle Salomé, and Christian David. High-efficiency fresnel zone plates for hard X-rays by 100 keV e-beam lithography and electroplating. *Journal of Synchrotron Radiation*, 18(3):442–446, 2011. ISSN 09090495. doi: 10.1107/S0909049511002366.
- M. Guizar-Sicairos, A. Diaz, M. Holler, M. S. Lucas, A. Menzel, R. A. Wepf, and Oliver Bunk. Phase tomography from x-ray coherent diffractive imaging projections. *Optics Express*, 19(22):21345, 2011. ISSN 1094-4087. doi: 10.1364/OE.19.021345.
- M. Guizar-Sicairos, I. Johnson, A. Diaz, M. Holler, P. Karvinen, H-C. Stadler, R. Dinapoli, Oliver Bunk, and Andreas Menzel. High-throughput ptychography using Eiger-scanning X-ray nano-imaging of extended regions. *Optics Express*, 22(12):14859, 2014. ISSN 1094-4087. doi: 10.1364/OE.22.014859.
- M. Guizar-Sicairos, J.J. Boon, K. Mader, A. Diaz, and A. Menzel. Quantitative interior x-ray nanotomography by a hybrid imaging technique. *Optica*, 2(3):259–266, 2015.
- J. Gutiérrez, A. Mas, E. Gil, and V. Galvañ. Clay-related damage in rainscreen walls built with natural stone coverings. *Construction and Building Materials*, 29:357–367, 2012. ISSN 09500618. doi: 10.1016/j.conbuildmat.2011.10.060.
- T. Harjupatana, J. Alaraudanjoki, and M. Kataja. X-ray tomographic method for measuring three-dimensional deformation and water content distribution in swelling clays. *Applied Clay Science*, 114:386–394, sep 2015. ISSN 01691317. doi: 10.1016/j.clay.2015.06.016.

- M. Holler, A. Diaz, M. Guizar-Sicairos, P. Karvinen, E. Färm, E. Härkönen, M. Ritala, A. Menzel, J. Raabe, and O. Bunk. X-ray ptychographic computed tomography at 16 nm isotropic 3D resolution. *Scientific reports*, 4:3857, jan 2014. ISSN 2045-2322. doi: 10.1038/srep03857.
- L. Holzer, F. Indutnyi, P. H. Gasser, B. Münch, and M. Wegmann. Three-dimensional analysis of porous BaTiO₃ ceramics using FIB nanotomography. *Journal of microscopy*, 216(Pt 1):84–95, oct 2004. ISSN 0022-2720. doi: 10.1111/j.0022-2720.2004.01397.x.
- M. R. Howells, T. Beetz, H. N. Chapman, C. Cui, J. M. Holton, C. J. Jacobsen, J. Kirz, E. Lima, S. Marchesini, H. Miao, D. Sayre, D. a. Shapiro, J. C H Spence, and D. Starodub. An assessment of the resolution limitation due to radiation-damage in X-ray diffraction microscopy. *Journal of Electron Spectroscopy and Related Phenomena*, 170(1-3):4–12, 2009. ISSN 03682048. doi: 10.1016/j.elspec.2008.10.008.
- X. Huang, H. Yan, R. Harder, Y. Hwu, I. K. Robinson, and Y. S. Chu. Optimization of overlap uniformness for ptychography. *Optics express*, 22(10):12634–12644, 2014. ISSN 1094-4087. doi: 10.1364/OE.22.012634.
- L. M. Keller, P. Schuetz, R. Erni, M. D. Rossell, F. Lucas, P. Gasser, and L. Holzer. Characterization of multi-scale microstructural features in Opalinus Clay. *Microporous and Mesoporous Materials*, 170:83–94, apr 2013. ISSN 13871811. doi: 10.1016/j.micromeso.2012.11.029.
- W. D. Keller. Kaolinization of feldspar as displayed in scanning electron micrographs. *Geology*, 6(march):184–188, 1978. doi: 10.1130/0091-7613(1978)6<184.
- R. A. Ketcham and W. D. Carlson. Acquisition, optimization and interpretation of X-ray computed tomographic imagery: applications to the geosciences. *Computers & Geosciences*, 27(4):381–400, 2001.
- P. Kraft, A. Bergamaschi, C. Bronnimann, R. Dinapoli, E. F. Eikenberry, H. Graafsma, B. Henrich, I. Johnson, M. Kobas, A. Mozzanica, C. M. Schleputz, and B. Schmitt. Characterization and calibration of PILATUS detectors. *IEEE Transactions on Nuclear Science*, 56(3):758–764, 2009. ISSN 00189499. doi: 10.1109/TNS.2008.2009448.
- J. J. Lombardo, R. A. Ristau, W. M. Harris, and W. K. S. Chiu. Focused ion beam preparation of samples for X-ray nanotomography. *Journal of*

- synchrotron radiation*, 19(Pt 5):789–96, sep 2012. ISSN 1600-5775. doi: 10.1107/S0909049512027252.
- P. E. Øren and S. Bakke. Process based reconstruction of sandstones and prediction of transport properties. *Transport in Porous Media*, 46(2-3): 311–343, 2002.
- J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, C. Rueden, S. Saalfeld, B. Schmid, J-Y. Tinevez, D. J. White, V. Hartenstein, K. Eliceiri, P. Tomancak, and A. Cardona. Fiji: an open-source platform for biological-image analysis. *Nature Methods*, 9(7):676–682, 2012. doi: <http://dx.doi.org/10.1038/nmeth.2019>.
- E. Sebastián, G. Cultrone, D. Benavente, L. Linares Fernandez, K. Elert, and C. Rodriguez-Navarro. Swelling damage in clay-rich sandstones used in the church of San Mateo in Tarifa (Spain). *Journal of Cultural Heritage*, 9(1):66–76, 2008. ISSN 12962074. doi: 10.1016/j.culher.2007.09.002.
- J-P. Suuronen, M. Matuszewicz, M. Olin, and R. Serimaa. X-ray studies on the nano- and microscale anisotropy in compacted clays: Comparison of bentonite and purified calcium montmorillonite. *Applied Clay Science*, 101:401–408, nov 2014. ISSN 01691317. doi: 10.1016/j.clay.2014.08.015.
- P. Thibault and M. Guizar-Sicairos. Maximum-likelihood refinement for coherent diffractive imaging. *New Journal of Physics*, 14, 2012. ISSN 13672630. doi: 10.1088/1367-2630/14/6/063004.
- P. Thibault, M. Dierolf, O. Bunk, A. Menzel, and F. Pfeiffer. Probe retrieval in ptychographic coherent diffractive imaging. *Ultramicroscopy*, 109(4): 338–43, mar 2009. ISSN 0304-3991. doi: 10.1016/j.ultramic.2008.12.011.
- S. Tomioka, T. Kozaki, H. Takamatsu, N. Noda, S. Nisiyama, N. Kozai, S. Suzuki, and S. Sato. Analysis of microstructural images of dry and water-saturated compacted bentonite samples observed with X-ray micro CT. *Applied Clay Science*, 47(1-2):65–71, jan 2010. ISSN 01691317. doi: 10.1016/j.clay.2008.09.001.
- K. E. Van Den Abeele, J. Carmeliet, P. A. Johnson, and B. Zinszner. Influence of water saturation on the nonlinear elastic mesoscopic

- response in Earth materials and the implications to the mechanism of nonlinearity. *Journal of Geophysical Research*, 107:1–11, 2002.
- M. van Heel and M. Schatz. Fourier shell correlation threshold criteria. *Journal of structural biology*, 151(3):250–62, sep 2005. ISSN 1047-8477. doi: 10.1016/j.jsb.2005.05.009.
- T. Wangler and G. W. Scherer. Clay swelling mechanism in clay-bearing sandstones. *Environmental Geology*, 56(3-4):529–534, may 2008. ISSN 0943-0105. doi: 10.1007/s00254-008-1380-3.
- T. P. Wangler, A. Stratulat, P. Duffus, J. H. Prévost, and G. W. Scherer. Flaw propagation and buckling in clay-bearing sandstones. *Environmental Earth Sciences*, 63(7):1565–1572, 2011. ISSN 18666280. doi: 10.1007/s12665-010-0732-y.
- D. Wildenschild and A. P. Sheppard. X-ray imaging and analysis techniques for quantifying pore-scale structure and processes in subsurface porous medium systems. *Advances in Water Resources*, 51(0):217–246, 2013. ISSN 0309-1708. doi: <http://dx.doi.org/10.1016/j.advwatres.2012.07.018>.
- E. M. Winkler. Frost damage to stone and concrete: geological considerations. *Engineering Geology*, 2(5):315–323, 1968.

6

Comparison between traditional laboratory tests, permeability measurements and CT-based fluid flow modelling for cultural heritage applications

In this chapter, a practical application of the data that were acquired using the experiments and techniques described in the previous chapters is demonstrated. Data obtained using μ CT will be compared to measurements and calculations of permeability and the capillary absorption rate of the sandstones under investigation, in order to find the correlation between pore network characteristics and fluid management characteristics of these sandstones. This chapter is based on a paper that has been submitted to Science of the Total Environment as *Comparison between traditional laboratory tests, permeability measurements and CT-based fluid flow modelling for cultural heritage applications for consideration to Science of the Total Environment*. - **Wesley De Boever**, Tom Bultreys, Hannelore Derluyn, Luc Van Hoorebeke, Veerle Cnudde. This paper has been submitted on the 14th of September 2015 and is

currently under review.

6.1 Introduction

The determination of the capillary absorption coefficient of natural stones according to European standard EN 1925 (1999) is standardised on blocks of around $(5\text{ cm})^3$. While this is convenient for the characterisation of stones prior to their use in construction, this is not so much the case for historical buildings. Nevertheless, when assessing the quality of a building stone in a historical monument, determination of the capillary absorption coefficient often is one of the standard tests. By comparing the coefficient of the weathered rock to that of the same or similar unweathered stones, the internal deterioration of the material can be estimated. Also for the validation of the effect of consolidation or hydrophobation (Tsakalof et al., 2007; Manoudis et al., 2009) of natural stones, the capillary absorption coefficient is an important measure (Peruzzi et al., 2003; Cnudde, 2005).

However, ancient buildings and monuments are precious, meaning that it is often difficult to acquire a large volume of sample material for petrophysical testing. In this case, tests would have to be done on smaller samples, inflicting as little damage as possible to the structure. European standard *EN 15801: Conservation of cultural property Test methods Determination of water absorption by capillarity (2010)* describes a method for the determination of the capillary absorption coefficient by performing measurements on samples of at least $(10\text{ mm})^3$, in roughly the same way as the large-scale test. Although this is an adequate method for many materials, absorption in sandstones like the Bentheim sandstone is often too fast to be measured by weighing at different intervals.

In this chapter, we aim to correlate traditional fluid flow parameters such as the capillary absorption coefficient to the stone's permeability, a value that is usually not determined in weathering studies of buildings. The absolute permeability of a medium is described as a measure of the ability of this porous medium to allow fluids (liquid and gas) to pass through it. Permeability has different units, depending on the specific field in geology it is used in, although the official SI unit for permeability is m^2 . When dealing with reservoir rocks and fluid transport modelling, a more practical unit is used: the *darcy* (d) or *millidarcy* (md). A medium that has a permeability of 1 darcy permits a flow of 1 cm^3 per second, of a fluid

with a viscosity of 1 mPa·s under a pressure gradient of 1 atm/cm across an area of 1 cm². This corresponds to about 10⁻¹²m² or 1 μm². The definition of permeability (κ) is further expressed by Darcy's law:

$$\kappa = v \frac{\mu \Delta x}{\Delta P} \quad (6.1)$$

In this equation, v is the velocity of fluid flow in m/s through the medium, μ is the viscosity of the fluid that is flowing in Pa·s, ΔP is the applied pressure drop over the medium in Pa and Δx is the thickness over which permeability is measured in m. Rocks with a high permeability generally have a high porosity and a high connectivity between the pores and permeability is mainly hindered by narrow pore throats. Comparably, high porosity and good connectivity through large throats also give rise to high capillary absorption coefficients, with the difference that narrow capillary tubes provide more capillary suction (Hall and Hoff, 2002), and therefore increase the maximum rise height of fluids by capillarity (Karoglou et al., 2005). Since similar stone properties are responsible for both processes, in-situ permeability measurements of the permeability directly on a building or outcrop might be directly correlated to laboratory measurements of the capillary absorption coefficient, since both parameters tell us something on how fast a fluid can flow through a building stone.

Furthermore, the obtained measurements and results can be corroborated by using fluid flow modelling directly on 3D μCT image data (Mostaghimi et al., 2013) or on pore network models extracted from these images (Dong and Blunt, 2009; Bultreys et al., 2015). By studying the pore network of the investigated materials, we aim to link differences in structure and connectivity of their pore network to differences in the capillary absorption coefficient. Furthermore, this data will be used to explain the correlation between capillary absorption and permeability in the investigated samples. By understanding these relations, both the water management and weathering behaviour of stones could be predicted in the future, without having to analyse a large quantity of samples. Experiments were performed on three kinds of Bentheim sandstone: the Bentheim variety and two varieties of the Gildehaus type, called the 'regular' and the 'porous' variety. As the names suggest, the main difference between these two types is the slightly higher porosity in the porous variety compared to regular variety. Both varieties belong to the Gildehaus type of Bentheim sandstone, and their difference in porosity is only affected by local

heterogeneities. The names have been chosen since the regular samples' porosity lies closer to the overall average of the Gildehaus variety of Bentheim sandstone. Since the mineralogy of the three Bentheim varieties is very similar, differences in water management properties can be addressed mainly to the differences in pore network characteristics and not to chemical variations. Besides the Bentheim sandstones, several other stones were included in the test, in order to understand the relations in a more general way. These materials are the French Vosges sandstone (De Boever et al., 2015), German Oberkirchner (Nijland et al., 2003) and Leistadter sandstones, and a few Belgian building stones: a glauconite-rich sandstone called Fieldstone, the ferruginous sandstone of Diest (Cnudde et al., 2011), and Maastricht limestone (Cnudde, 2005).

This chapter starts with a discussion on experimental results of capillary absorption and in-situ air permeability. Subsequently, CT scans performed on small sub-samples of the analysed stones will be presented, followed by fluid flow simulations and characterisation of the pore network on these 3D datasets. Before making any conclusions, an estimation of the representativeness of these small CT sub-volumes will be shown, to evaluate if the obtained characteristics and simulations are representative for larger rock volumes. Results of capillary absorption, permeability measurements and the CT-based methods are then discussed and compared, to assess the degree of correlation between the three types of measurements. Based on these conclusions, the possibility of using CT-based permeability simulations and in-situ air permeability measurements in cultural heritage applications is discussed.

6.2 Methods

6.2.1 Microscopic experiments and analysis

For all materials, except the Vosges sandstone, a sample with a diameter of around 5 mm was scanned using HECTOR. A tube voltage of 100 kV was used and 2400 projections with 1 second exposure time were taken. This resulted in datasets with a reconstructed voxel size of around 5 μm . This resolution does not provide enough detail for correct analysis of the Vosges sandstone, and therefore the high-resolution dataset from chapter 4 that was acquired at the Medusa setup was used. This dataset has a spatial

voxel size of $0.86\ \mu\text{m}$. All volumes were segmented into binary datasets representing the pore space and solid matrix using Octopus Analysis. Several properties of a pore network can be considered important for the water flow characteristics of a stone. To determine the properties of the pore system, geometrical pore network models (PNMs) were extracted from each CT scan (Dong and Blunt, 2009). In these representations of the pore space, each pore body is presented as a sphere which is connected to other pores by tubes (figure 6.1). These spheres and tubes are typically called nodes and links. Besides the overall open porosity and percolating porosity, one of the main properties of a pore network is the connectivity of the pores. A frequently used way of expressing this is the so called coordination number (CN). This CN represents the number of other pores a given pore is connected to, and the average CN of the entire network can be seen as a measure for the networks connectivity. Two other important parameters determining flow in porous media are the size of the pores, or the pore body size, and the size of the pore throats forming the connections between different pores. The simplified, conceptual representation of the pore space by a pore network model allows a comprehensive analysis of the differences between different pore systems, as the connectivity, node size and link size are numbers that are easily determined.

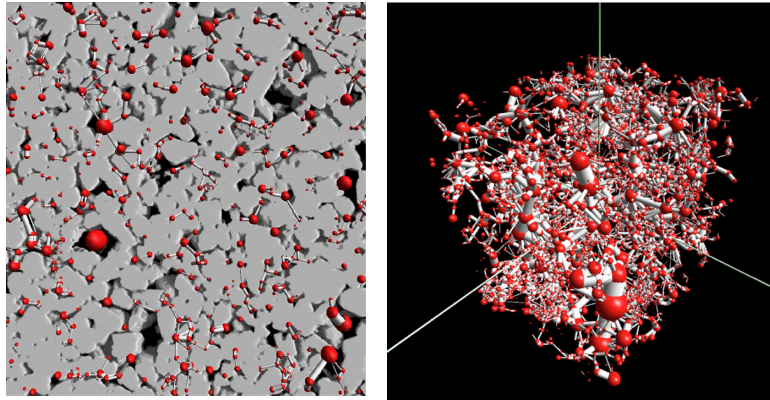


Figure 6.1: Left: Example of a pore network model, extracted from a segmented micro-CT scan of a Bentheim sandstone. Pore bodies are represented by spheres, the links between them as cylinders. Right: Relation of pore network model to the micro-CT volume. The size of the spheres and cylinders represent the size of the pore bodies and the thickness of the connections.

Network extraction was performed using segmented, binary CT datasets representing the pore space and solid matrix as an input for the extraction

algorithm. The first step is a grain-recognition algorithm, separating the solid matrix into individual grains. Thereafter, these grains are dilated until there is no pore space left. From this ultimately dilated dataset, a skeleton of the pore space can be constructed (Bakke and Øren, 1997) by placing skeleton voxels where 3 ultimately dilated grain surfaces meet. Points on this skeleton where 4 or more ultimately dilated grains meet are determined to be nodes in the network. From the obtained skeleton, a pore network can be built by determining the volume of the nodes and the diameter of the narrowest constrictions in the throats, based on the segmented micro-CT scan. The method developed by Bakke and Øren employs a rotating vector method to scan the surfaces perpendicular to the skeleton line, in order to find the volume and the inscribed sphere radius in each pore. A similar vector scanning method is used to find the narrowest constrictions between pores. The pore networks for these experiments were extracted using e-Core, developed by FEI (Norway).

The permeability of the studied stones was calculated on the pore scale by performing fluid flow modelling on the data acquired by CT. This can either be done by direct modelling on the images or by modelling transport on the earlier obtained PNMs. Direct modelling on the images was performed using the Lattice-Boltzmann method. This method solves a discretised Boltzmann equation of fluid-particle distributions that move and interact on a regular lattice, imposing a finite number of possible movement directions (Ramstad et al., 2009). At each node of this lattice, a particle distribution for each possible particle velocity vector is defined and the number of these vectors is limited by only allowing particles to move to a neighbouring node in one simulation time step. Since the lattice is usually defined by the voxel grid of the 3D CT dataset, no meshing is involved in this simulation method and calculations are done directly on the segmented images. Solid boundaries are typically handled with a simple bounce-back condition, meaning a package of particles which hit a solid wall node at a certain time step are bounced back to the node in the pore space where they came from (Llewellyn, 2010). It can be shown that the Navier-Stokes equations can be recovered from the lattice-Boltzmann scheme in the incompressible limit. This direct calculation of permeability generally gives reliable results compared to experimental data, especially in stones where pores are big enough to be resolved properly and Lattice-Boltzmann simulations are generally more accurate than PNM-based permeabilities (see below). Permeability can also be calculated by modelling fluid flow on the PNMs discussed earlier. The

reason to do so is that due to computational demands, direct modelling is sometimes difficult or impossible in rocks with broad pore size distributions and complicated structures. PNM simulations on the other hand, are much more computationally efficient. To calculate the permeability, the flow rate through the network is calculated by imposing a pressure difference over the network and assuming mass conservation of the fluids in each pore. This leads to a set of linear equations which can be solved for the fluid pressure in each pore:

$$q_{ij} = g_{ij}(P_i - P_j) \sum_j q_{ij} = 0, \forall i \quad (6.2)$$

with q_{ij} the flow from pore i to pore j , g_{ij} the hydraulic conductivity between pores i and j and P_j the pressure in pore j . The connecting throat between two pores can be assumed to be for example cylindrical, in which case Hagen-Poiseuilles law provides an analytical expression of the conductivity g_{ij} in function of the throat length and diameter:

$$g_{ij} = \frac{\pi R_{ij}^4}{8\mu L_{ij}} \quad (6.3)$$

With L_{ij} the distance from pore i to pore j , R_{ij} the inscribed radius of the throat connecting pores and μ the fluid viscosity. Solving equation 6.2 yields the volumetric flow rate through each pore in the outlet face of the network, from which the total flux Q through this face can be calculated. If this flux is multiplied by the viscosity and divided by the applied pressure gradient, the network permeability is found.

6.2.2 Macroscopic experiments

Water uptake experiments on the stones were performed following EN 1925 (1999) on $(5 \text{ cm})^3$ blocks of each material, as described in chapter 1. The tests were continued for 2 days after the absorption reached a plateau.

Permeability of rocks and sediments is usually measured in a triaxial testing cell in a specialised petrophysics lab. Although this gives the most reliable results, it also requires rather large samples of several centimetre in diameter and height. Therefore, direct measurement of the permeability using a portable gas permeameter was done, using the TinyPerm II (www.ner.com). This device is pressed against the surface that needs to be

measured, and using a plunger, a vacuum is created in the nozzle of the device. The time it takes for this vacuum to restore, by transport of air through the material, is a measure for the permeability of the stone. Using the correct conversion formula, TinyPerm values can be converted into absolute permeability values in md (Brown and Smith, 2013). A disadvantage of these types of measurements is that permeability in many stones and sediments (Huysmans et al., 2008) tends to vary on a very local scale. This problem also occurs when measuring capillary absorption, especially using the cultural heritage standard, and can be improved by averaging out measurements on a larger area of a stone.

6.3 μ CT analysis

For Bentheim sandstone, all three stones were scanned at exactly the same settings, resulting in datasets with a reconstructed voxel size of 5.24 μm . The segmented volumes had a porosity of 24 % and 21 % for the porous and regular varieties of the Gildehaus type of Bentheim sandstone, and 17 % for the Bentheim type. In all samples, almost the entire porosity was classified as open porosity, meaning that the Bentheim sandstone has a very open and connected pore structure. The porous variety of the Gildehaus type Bentheim is recognisable by the high amount of minerals which are highly attenuating to X-rays, and most probably correspond to zircons (figure 6.2). The porosity of Vosges sandstone was found to be 16.50 %, with an open porosity of 16.3 %. Unlike Bentheim sandstone, various different mineral phases and pore sizes are present in these 3D images. Maastricht limestone has the highest porosity of the remaining stones, at 39.60 %. The other materials also have rather high porosity values, ferruginous sandstone has a porosity of 20.23 %. In the scans of this material, quartz (lowest grey values) can be clearly separated from glauconite (intermediary grey values) and iron oxides (highest grey values). Fieldstone has a porosity of 18.16 %. It consists out of quartz (low grey values) and glauconite (high grey values). Oberkirchner sandstone has a porosity of 15.13 % and consists mostly out of quartz. The Leistadter sandstone has the lowest porosity value of the analysed stones, at only 7.77 %.

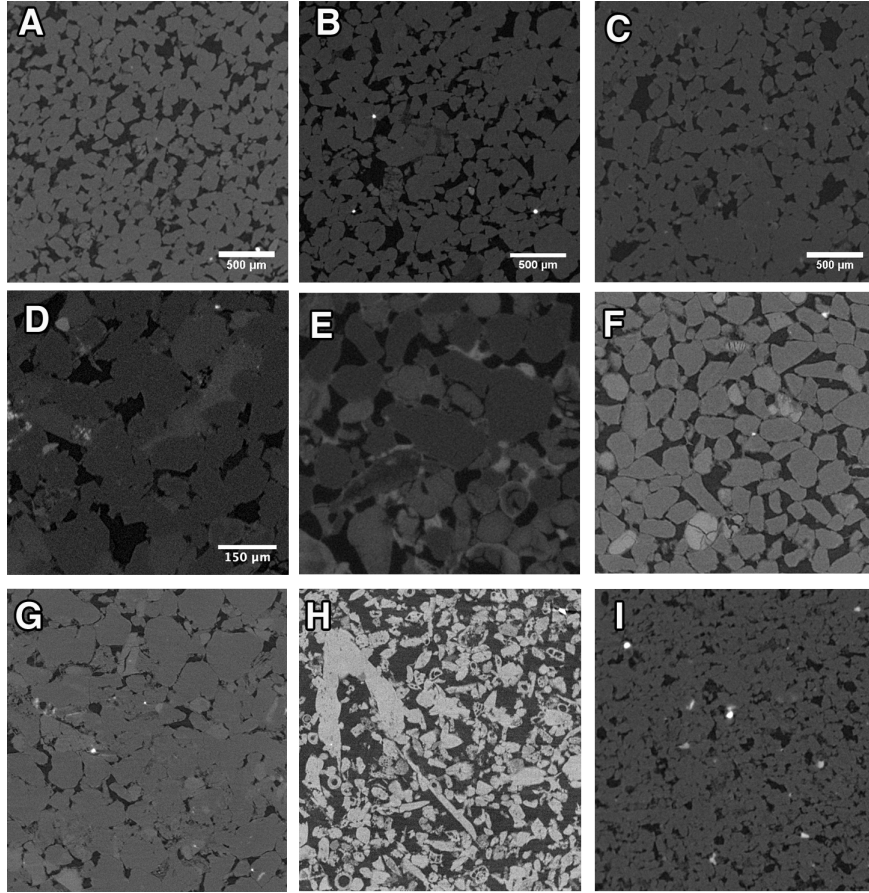


Figure 6.2: Details of CT slices through the analysed stones. A: Regular Gildehaus type Bentheim, B: Porous Gildehaus type Bentheim, C: Bentheim type Bentheim, D: Vosges, E: Ferruginous sandstone, F: Fieldstone, G: Leistadter sandstone, H: Maastricht limestone, I: Oberkirchner sandstone

6.4 Representative elementary volume estimation.

Although for cultural heritage applications, smaller samples are always better than larger samples to create as little damage as possible, the analysed volume should be representative in order to draw correct conclusions. In order to evaluate if the analysed samples were large enough, an REV estimation using the two-point-correlation function or autocorrelation function (Ioannidis et al., 1996) of the binary datasets was performed. The two-point-correlation function is defined as the probability

that both ends of a randomly oriented and placed line segment with a given length r are both in the same phase in a binary volume. While this two-point-correlation function only depends on r for isotropic materials, one-dimensional two-point-correlations functions parallel to x, y or z can be calculated for anisotropic media (Rozenbaum and Du Roscoat, 2014). Differences between the one-dimensional two-point-correlation functions in different directions provide information about a samples anisotropy. For bigger values of r , the two-point-correlation function will drop and eventually reach zero (figure 6.3). The length where this happens is called the correlation length l_c , and beyond this length scale, there are no more correlations in the dataset (Rozenbaum and Du Roscoat, 2014). As the correlation length is an estimation of the size of the largest structures in the binary dataset, a volume with a side length which is one order of magnitude larger than this length is often a good estimation of the sample's REV. Note that this REV estimation is limited to the application of porosity and pore network analysis, since it does not take the distribution of different mineral phases into account. Furthermore, larger-scale variations such as layering of a stone in the centimetre-scale range cannot be taken into account since the resolution of μ CT at these sample sizes would not allow quantitative assessment of the porosity.

All 2-point-correlation functions were calculated using e-Core. The l_c values of the Bentheim samples analysed in this work varied between $\pm 110 \mu\text{m}$ for the regular Gildehaus type Bentheim and $\pm 160 \mu\text{m}$ for the Bentheim type (table 6.1). This means that in terms of porosity-analysis, the minimum sample diameter of Bentheim sandstone lies between 1.1 and 1.5 mm, which is far below the size of the analysed volume of $(2500 \mu\text{m})^3$. The correlation length of Vosges sandstone lies around $160 \mu\text{m}$, meaning that a sample size of 1.6 mm would be needed for a representative sample. Although the scanned sample is a cylinder with a diameter of 1 mm, pore network extraction was performed on a cuboid sample with a side length of $\pm 600 \mu\text{m}$, meaning that the analysed pore network is actually too small. Analysing a larger sample however is not an option in this case, since a high spatial resolution is needed in the case of the Vosges sandstone. The analysed sample is just around 5 times the correlation length, meaning that caution has to be taken when analysing the results. Of the other stones, only the Maastricht limestone has a sample size that is just under the minimum REV requirements (2.5 mm vs. 3.0 mm REV). The analysed volume of all other materials corresponded to the REV size or larger. The different one-dimensional

two-point-correlation functions show almost no variation, meaning that all of the analysed samples are isotropic at the studied scale.

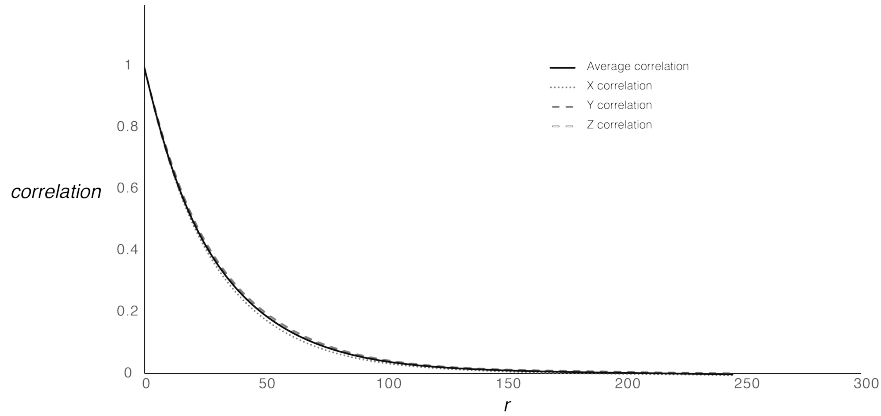


Figure 6.3: 2-point-correlation functions of the Bentheim sandstone, type Bentheim. Correlation reaches zero at around 160 μm . This 2-point-correlation function as calculated using e-Core.

Stone type	Correlation length	Minimum sample size	Analysed sample size
<i>Regular Gildehaus Bent.</i>	110 μm	1.1 mm	2.5 mm
<i>Porous Gildehaus Bent.</i>	140 μm	1.4 mm	2.5 mm
<i>Bentheim Bent.</i>	160 μm	1.6 mm	2.5 mm
<i>Vosges</i>	160 μm	1.6 mm	0.6 mm
<i>Oberkirchner</i>	170 μm	1.7 mm	3.2 mm
<i>Maastricht</i>	300 μm	3.0 mm	2.5 mm
<i>Ferruginous ss</i>	250 μm	2.5 mm	2.5 mm
<i>Fieldstone</i>	240 μm	2.4 mm	2.5 mm
<i>Leistadter</i>	180 μm	1.8 mm	2.5 mm

Table 6.1: Correlation lengths of all analysed stones. The values in bold point out the samples that are actually too small to be representative, but could not be made bigger due to the constraints of μCT .

6.5 Capillary uptake

A big difference exist between the capillary absorption values of the Bentheim and Gildehaus varieties of Bentheim and the Vosges sandstone. The average C values of the samples in these experiments were 46, 573 and $89 \text{ g}\cdot\text{m}^{-2}\cdot\text{s}^{-1/2}$. The porous variety of Gildehaus type Bentheim has an even higher capillary absorption coefficient of $703 \text{ g}\cdot\text{m}^{-2}\cdot\text{s}^{-1/2}$. Full saturation of the Gildehaus type of Bentheim sandstone happens in a matter of seconds, confirming that the cultural heritage method for determination of C (following EN 15801) would not be applicable to this kind of material. The Vosges sandstone has a capillary absorption coefficient that is a little higher than the Bentheim variety of Bentheim, at $89 \text{ g}\cdot\text{m}^{-2}\cdot\text{s}^{-1/2}$. The highest value of C was found in Maastricht limestone ($2394 \text{ g}\cdot\text{m}^{-2}\cdot\text{s}^{-1/2}$) while Fieldstone, Leistadter sandstone and Oberkirchner sandstones all have very low C values between 10 and $18 \text{ g}\cdot\text{m}^{-2}\cdot\text{s}^{-1/2}$. The ferruginous sandstone, finally, has a capillary absorption coefficient comparable to the Bentheim type Bentheim sandstone, at $40 \text{ g}\cdot\text{m}^{-2}\cdot\text{s}^{-1/2}$ (figure 6.2).

Material	C ($\text{g}\cdot\text{m}^{-2}\cdot\text{s}^{-1/2}$)
<i>Fieldstone</i>	10
<i>Leistadter</i>	14.8
<i>Oberkirchner</i>	17.3
<i>Ferruginous SS</i>	40
<i>Bentheim Bent.</i>	46
<i>Vosges</i>	89
<i>Regular Gildehaus Bent.</i>	573
<i>Porous Gildehaus Bent.</i>	703
<i>Maastricht</i>	2394

Table 6.2: Capillary absorption coefficient of the analysed stones.

6.6 Permeability

Table 6.3 shows the results of permeability calculations by pore scale modelling using Lattice-Boltzmann and PNMs and the results from

TinyPerm measurements. In most cases, measurements between the three methods correspond quite well, although in some cases there are substantial differences. The measurements using the TinyPerm II mostly result in higher permeabilities than the simulated data, but usually fall in the same order of magnitude as the latter. Especially for Leistadter sandstone and fieldstone, the difference is significant, which probably means that the connectivity and structure is not well captured in these μ CT scans. PNM-based permeability corresponds quite well with the more trustworthy Lattice-Boltzmann method in samples with a low-complexity pore system, such as the Bentheim sandstones and Ferruginous sandstone. In more complex situations such as Vosges sandstone there is a large difference in permeability values between these modelling methods.

Material	TinyPerm	Lattice-Boltzmann	PNM
<i>Fieldstone</i>	589	90.1	190
<i>Leistadter</i>	261	16.15	6.51
<i>Oberkirchner</i>	16.4	36	37
<i>Ferruginous SS</i>	1032	828	799
<i>Bentheim Bent.</i>	652	326	477
<i>Vosges</i>	146	120	14.2
<i>Regular Gildehaus Bent.</i>	3008	1146	1433
<i>Porous Gildehaus Bent.</i>	5011	4779	4156
<i>Maastricht</i>	19933	6310	11072

Table 6.3: Permeability of analysed stones using different methods (in md)

6.7 Pore network properties

While the μ CT datasets provide the total porosity, PNMs also provide a value for the percolating porosity, i.e. the pores that contribute to flow throughout the entire sample. While similar, this does not equal the open porosity, since pores at the edge of the sample with no further connection to the network are not taken into account. In the case of the well-connected stones with large-pores such as the Bentheim sandstone, total porosity is almost identical to the percolating porosity. Absolute results for network characteristics depend on the extraction method that was used, but since the same method was used for each material, results can be used here for

comparison between different materials.

For most samples, networks were extracted from a volume of $(2500\text{ }\mu\text{m})^3$, in order to allow for a correct comparison between the different types of stone. All network properties are listed in table 6.4. The average radius of the pore bodies in the porous Gildehaus type Bentheim shows that these pores are significantly bigger than in the other two types, explaining the higher porosity. This porous variety also has the highest average connectivity of all Bentheim types and the largest average link radius. For all types, very high maximum connectivities (58 to 76) have been measured. These values are unrealistic for a simple sandstone and are probably caused by oversegmentation in areas of the stone that are not clearly resolved at the spatial resolution of the μCT datasets, for example in the clay-rich areas of the stone. The size of CN distribution curves (figure 6.4) is quite similar for all Bentheim types. In terms of pore size distribution (figure 6.5), the porous Gildehaus type Bentheim has the broadest distribution and the largest pores, with a significant amount of pore bodies between 40 and 60 μm . Distributions of regular Gildehaus and Bentheim types of Bentheim are quite similar, and the shape of the curves suggests that most of the porosity is well-captured by the μCT data.

Analysis of the Vosges sandstone was performed on a much smaller volume of $716 \times 598 \times 688\text{ }\mu\text{m}^3$. The total and percolating porosity of this μCT dataset was lower than all of the Bentheim varieties, and due to the smaller volume the amount of analysed pores was also smaller, even if the higher amount of fine-grained features in Vosges sandstone create a high number of small pores. Average connectivity of the stone lies in between the Gildehaus and Bentheim types of Bentheim sandstone, but the maximum CN is increased strongly due to the high number of small pores (figure 6.4). The shape of the pore body size distribution for Vosges sandstone (figure 6.5) suggests that not all porosity is resolved properly, as there is a sharp cut-off at the left side of the distribution.

The connectivity distribution of Maastricht limestone looks similar to that of Bentheimer sandstone, with an even larger amount of high connectivity numbers, while the curves for the other materials resemble more the Vosges sandstone curve. Ferruginous sandstone, Fieldstone and Maastricht limestone show rather broad pore size distributions, generally between 0 and 40 μm in diameter. The distribution of Ferruginous sandstone also shows a large amount of pores larger than 40 μm . From the distributions of Leistadter and Oberkirchner sandstones, it is clear that the majority of

pores is smaller than 20 μm .

Material	Perc. porosity Vol. %	CN (Min/max)	Node radius μm (Min/max)	Link radius μm (Min/max)
<i>Reg. Gildehaus Bent.</i>	21.9	4.5 1 / 76	17.2 2.18 / 97.7	10.4 2.1 / 53.0
<i>Por. Gildehaus Bent.</i>	24.1	4.9 1 / 66	22.6 1.9 / 115.1	13.9 1.8 / 84.1
<i>Bentheim Bent.</i>	16.9	4.0 1 / 58	16.0 2.3 / 95.2	9.8 2.0 / 56.2
<i>Vosges</i>	15.9	4.3 1 / 111	4.5 0.5 / 42.0	3.1 0.3 / 24.0
<i>Oberkirchner</i>	10	3.3 1 / 38	10.6 2.3 / 62.9	6.8 2.2 / 42.6
<i>Maastricht</i>	39.1	5.6 1 / 142	15.4 2.1 / 182.7	10.2 2 / 57.2
<i>Ferruginous SS</i>	19.4	4 1 / 66	22.9 2.4 / 124.5	15.7 1.9 / 75.2
<i>Fieldstone</i>	17.8	3.5 1 / 17	18.7 1.4 / 55.1	11.2 1.3 / 34.9
<i>Leistadter</i>	6.2	3.0 1 / 62	13.9 2.2 / 59.3	8.5 2.0 / 37.1

Table 6.4: Pore network properties of analysed samples

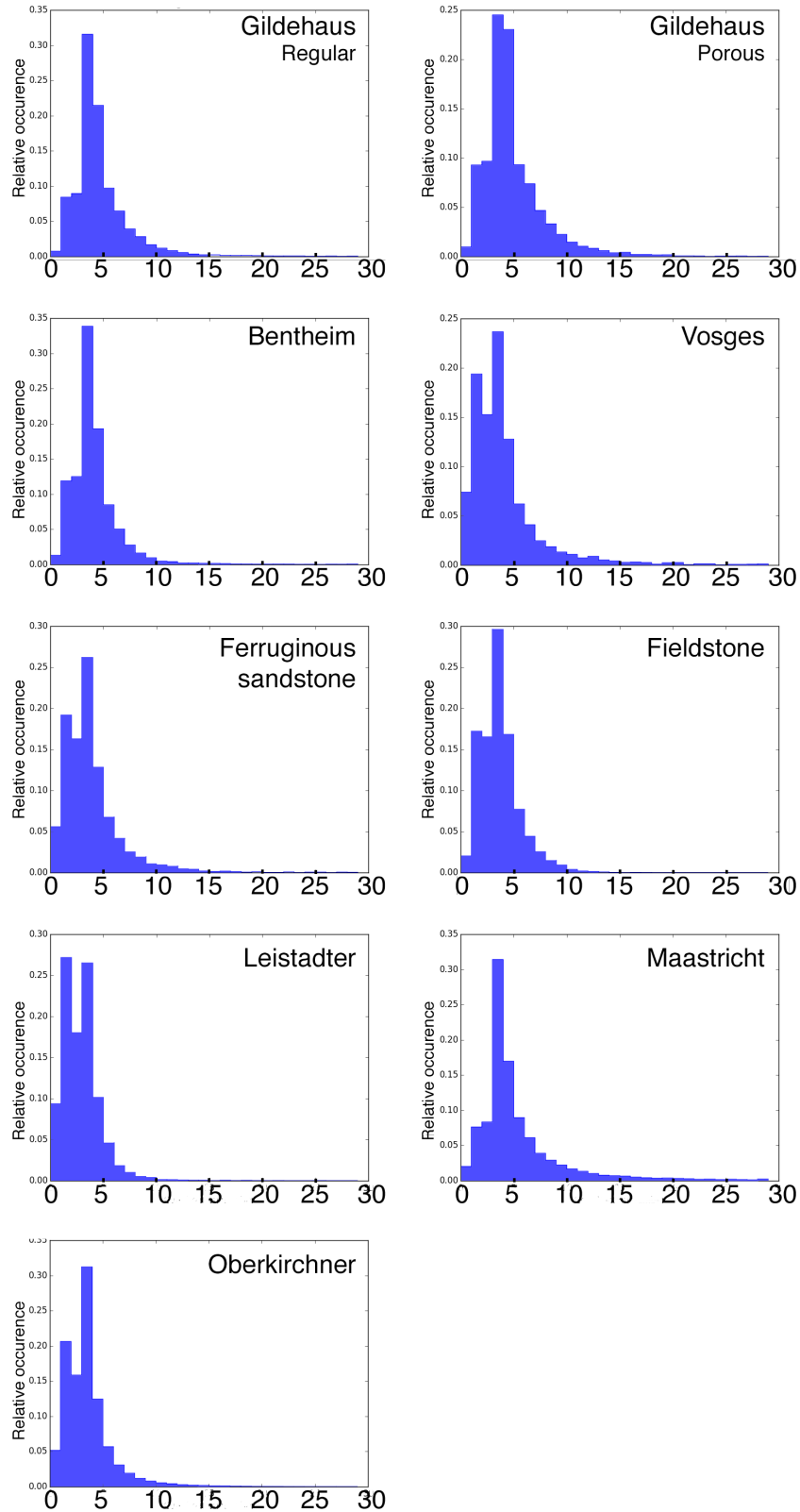


Figure 6.4: Distribution of coordination numbers, obtained by pore network extraction and normalised to 1. The coordination number size is displayed on the x-axis, relative frequency on the y-axis.

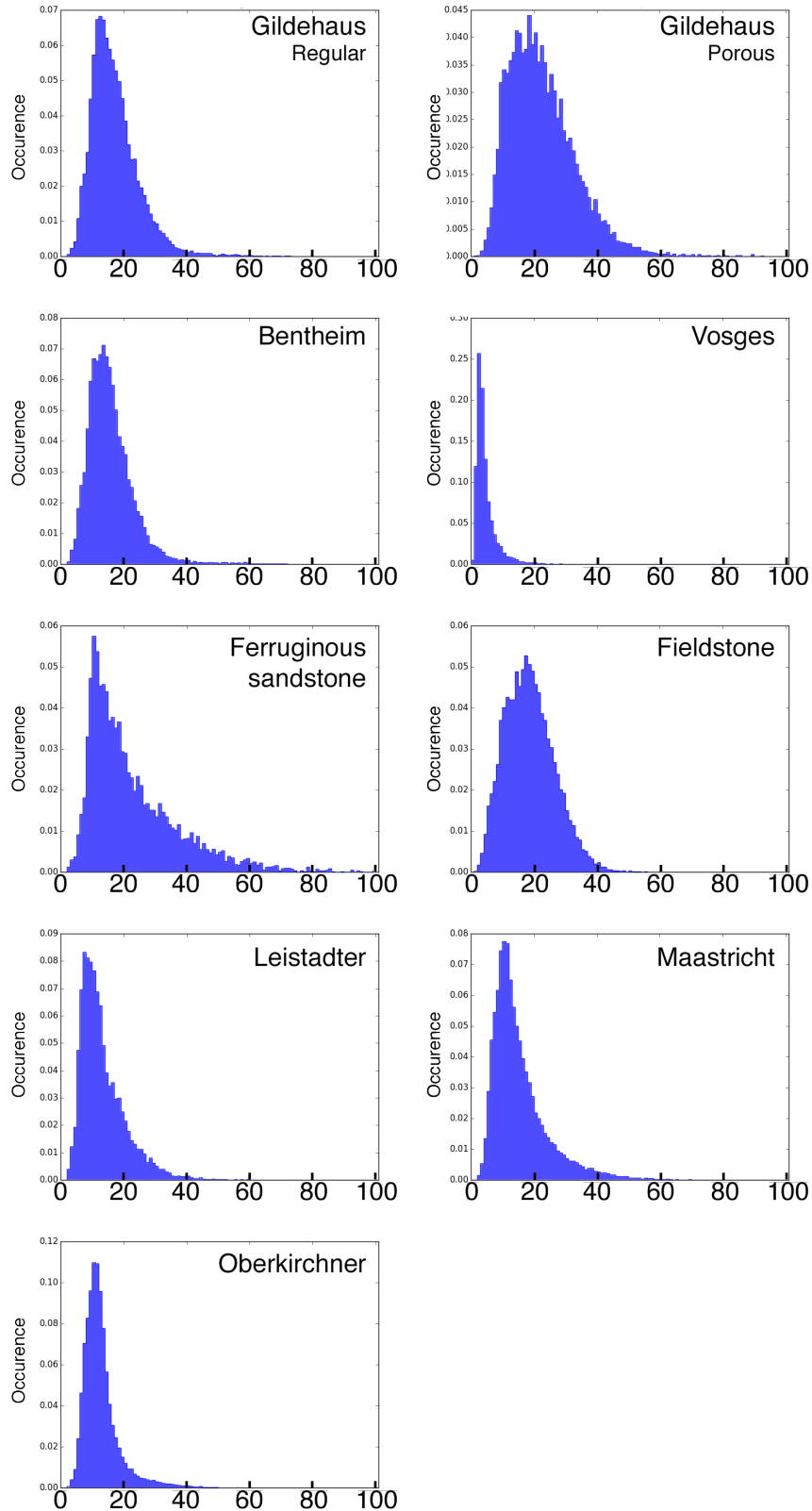


Figure 6.5: Distribution of the pore body sizes, obtained by pore network extraction and normalised to 1. Pore body size is displayed in micron on the x-axis, relative frequency on the y-axis.

6.8 Comparison between network properties, permeability and capillary absorption rate

In order to make an objective comparison between capillary absorption, pore network properties and permeability, the correlation between two parameters at a time is determined. The correlation gives a measure of how good two sets of data are linked to each other. To calculate the correlation r between two series of x and y points, the following equation can be used:

$$r_{xy} = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2}} \quad (6.4)$$

x_i and y_i are the values of parameter x and y and $\bar{x}$ and $\bar{y}$ are the mean values of these parameters. If the correlation between two sets equals 1, there is a perfect linear correlation, whereas there is no link between the two datasets if the correlation reaches 0. We must stress that the number of datapoints is not enough for a complete statistical analysis of the correlation. However, the costs and time restraints of μ CT do not allow for an analysis of hundreds of samples.

In the following discussion, the capillary absorption coefficient C will always be compared to another pore network property. For clarity, the samples are discussed in order of ascending C value, rather than in the order which the stones were discussed in earlier.

As can be seen in table 6.5, higher values of C occur at higher values of connectivity in the pore network. The only exception to this statement is in the case of Fieldstone, which has the lowest value for C but the third lowest value of connectivity. A high connectivity in the network will thus be beneficiary for capillary absorption. Although this rising trend can be observed, C does not rise linearly corresponding to the CN, resulting in a correlation of only 0.84. Table 6.5 also shows the values of percolating porosity that resulted from the PNM extraction of the different stones. Although a higher percolating porosity is expected to result in higher values of C , this relationship is less pronounced. The high porosity values but low C values of Fieldstone and ferruginous sandstone confirm this. The correlation value for C versus the percolating porosity reaches 0.90 (figure 6.6). However, taking into account the average coordination number of a network as a sort of correcting factor can result in a better

correlation between both parameters. Multiplying the percolating porosity with the coordination number and plotting this against C results in a correlation of 0.95 (figure 6.7). While this indeed seems to improve the correlation between the investigated parameters, further investigation on a larger number of samples should be performed to allow generalization of the results.

Material	C ($\text{g}\cdot\text{m}^{-2}\cdot\text{s}^{-1/2}$)	Connectivity	Percolating porosity (Vol.%)
<i>Fieldstone</i>	10	3.5	17.8
<i>Leistadter</i>	14.8	3.04	6.2
<i>Oberkirchner</i>	17.3	3.3	10
<i>Ferruginous SS</i>	40	4	19.4
<i>Bentheim Bent.</i>	46	3.98	16.9
<i>Vosges</i>	89	4.31	15.9
<i>Regular Gildehaus Bent.</i>	573	4.51	21.9
<i>Porous Gildehaus Bent.</i>	703	4.87	24.1
<i>Maastricht</i>	2394	5.6	39.1

Table 6.5: Capillary absorption coefficient compared to pore network properties of the analysed stones.

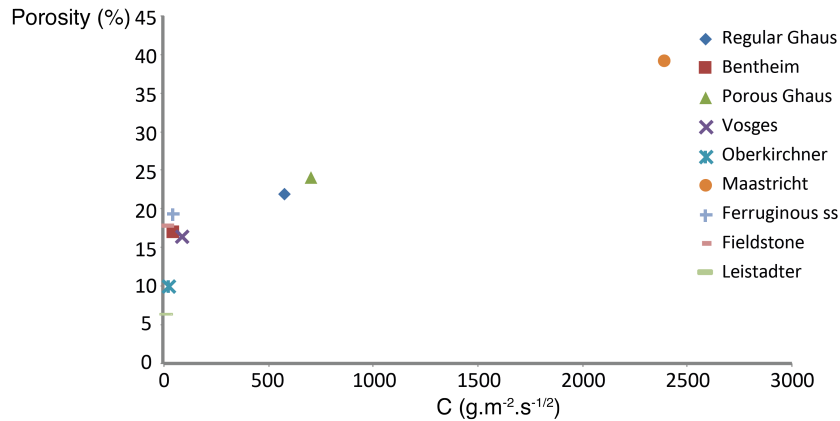


Figure 6.6: Plot of the capillary absorption coefficient C vs percolating porosity. The correlation coefficient is 0.90 (1 represents a linear relation).

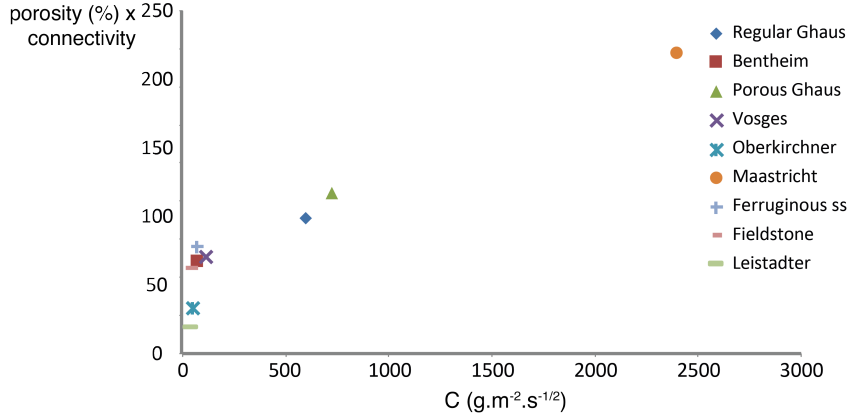


Figure 6.7: Plot of the capillary absorption coefficient C vs percolating porosity multiplied by connectivity. The correlation coefficient is 0.95 (1 represents a linear relation).

The different ways of measuring the permeability were strongly correlated to the capillary absorption coefficients in the investigated samples (table 6.4). Correlation between C and Lattice-Boltzmann permeability was found to be 0.91, and between C and PNM-determined permeability 0.99. While the Lattice-Boltzmann permeability should theoretically be more accurate, better results were thus obtained using pore network models. The main reason for this large difference is the rather low permeability that was found for the Maastricht limestone using the Lattice-Boltzmann method, being 'only' 6310 md. This value is significantly lower than TinyPerm and network permeabilities, and also lower than what we would expect based on the porosity and pore size distribution of the Maastricht limestone. The reason for this difference is somewhat unclear, since both the Lattice-Boltzmann simulation and pore network extraction were based on exactly the same dataset.

Correlation between the TinyPerm measurements and capillary absorption experiments is equally good, with a correlation coefficient of 0.993 (figure 6.8). This suggests that on-site permeability measurements are a possible alternative to destructive sampling and testing of the stones in a cultural heritage monument or building. The good correlation can be explained by the fact that both permeability and capillary absorption rely on high porosity and good connectivity in a rock's pore system, as was shown

earlier in this section. To validate this statement, correlation between permeability and the porosity multiplied with connectivity was checked, which yielded the exact same value as when capillary absorption was compared to the same parameters: a correlation of 0.94 (figure 6.9).

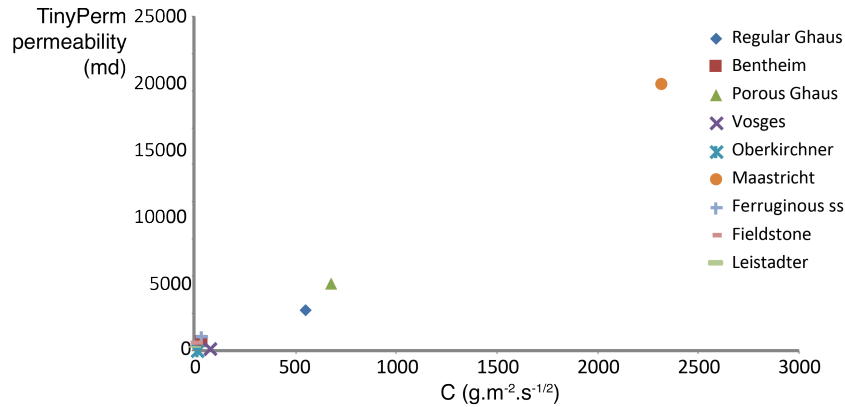


Figure 6.8: Plot of the capillary absorption coefficient C vs TinyPerm permeability. The correlation coefficient is 0.99 (1 represents a linear relation).

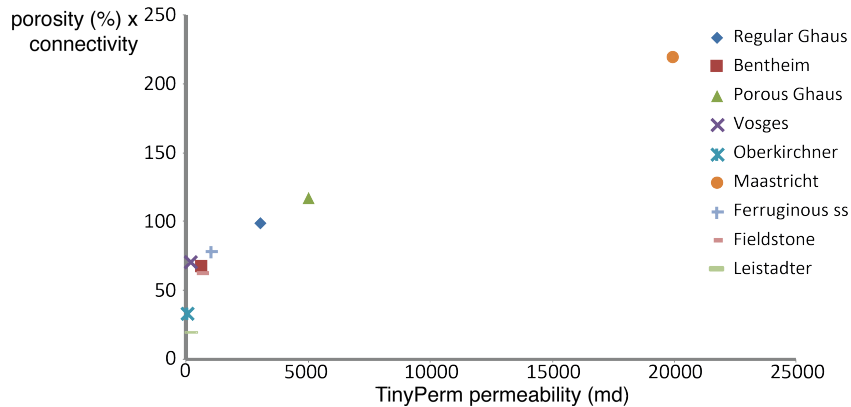


Figure 6.9: Plot of the TinyPerm permeability vs percolating porosity multiplied by connectivity. The correlation coefficient is 0.94 (1 represents a linear relation).

However, since permeability is driven by the connectivity of the larger pores in a network and capillary absorption is driven by small connections (Hudec, 1989), there are some unexpected results. The permeability of the Vosges sandstone for example is lower than expected from capillary

absorption experiments (figure 6.8). Despite the stone's rather high porosity, all three ways of determining the permeability resulted in these rather low values, and pore network based modelling even resulted in an extremely low value. A cause for this non-linear behaviour is to be sought in the structure and composition of the Vosges sandstone. The material's high porosity is created by the existence of larger pores of 100 - 200 μm in diameter, but the connections are often blocked by the high amount of fine-grained minerals inside the Vosges sandstones. Similar effects are to be expected in other rocks with high porosity, average to good connectivity, but narrow pore throats. For this kind of materials, network permeability could approximate real permeability values better through the extraction of multi-scale pore network models, including the microporosity in the network (Bultreys et al., 2015).

6.9 Conclusions

Capillary absorption tests have been widely accepted and standardised as a testing procedure for natural stones in cultural heritage applications. The methods described in this chapter provide promising alternatives in order to reduce the size and amount of samples needed, or even to completely make sampling redundant. Direct in-situ measurement of a rocks permeability using a portable air permeameter provided data that show excellent correlation with capillary absorption coefficients. Furthermore, both the interpretation and the measurement of permeability are easier for permeability than for the capillary absorption coefficient. Although correlation is evidently not perfect, permeability measurements may provide a valuable alternative to capillary absorption experiments in the future, especially for extremely valuable monuments or when results are needed in a very short time frame. Prerequisites for a more standardised and generally accepted use of permeameter measurements are however a larger-scale validation of the method over a broader range of stones and a larger number of samples. It is currently also unclear if both the capillary absorption coefficient and permeability have the same relation to weathering of the stone, and which of those parameters is actually better to assess the degree of weathering. This response will likely depend on the type of weathering, and whether it will cause a more closed or a more open pore network (Dewanckele et al., 2014).

In the case of the samples analysed in this chapter, an explanation for the good correlation could be provided by using X-ray tomography. Most of the samples possess rather large pores, that could be imaged by using X-ray computed tomography, on a large-enough sample size. Analysis of the μ CT data showed that the highest capillary absorption coefficients were observed in materials with high average connectivity in the network, especially if this high connectivity goes together with a high porosity percentage. The presence of pore- and throat-clogging minerals such as clays can decrease the permeability, causing it to be lower than expected based on the capillary absorption coefficient. It will therefore be necessary to have some preliminary knowledge on the material that is under investigation in order to compare portable air permeameter results to capillary absorption results. Since most historical buildings and their stones have been well characterised in numerous studies in the past, this condition is fulfilled in most cases.

Future investigation of this topic should clarify a number of issues, before this method can be used in the field. A large number of samples needs to be investigated, too see if the results are consistent. Special attention has to be paid to the inclusion of materials with an intermediary capillary absorption coefficient, between 100 and 500 $\text{g}\cdot\text{m}^{-2}\cdot\text{s}^{-1/2}$. Furthermore, more complex limestones should be included in the test, since many historical monuments in Europe are constructed using the limestones that are found in the area. For most limestones, validation of the results using μ CT and pore network modelling will be more difficult, since they tend to have more complex pore networks and a higher degree of microporosity. On the other hand, this validation would also be more important to understand the results for these rocks. Since capillary absorption coefficients are often used to check the quality or effectiveness of special treatments on a stone surface, such as consolidation, research should be done to verify if the change in a material's permeability after treatment is comparable to the change in capillary absorption rate.

We have shown the potential of in-situ permeability measurements for cultural heritage applications, as a possible alternative to capillary absorption experiments or to provide additional information about a material's condition. Both parameters show excellent correlation, based on the amount of samples that was included in our experiments, and this correlation could be explained by investigating the microstructural properties of these materials using 3D μ CT data. Furthermore, the added

value of pore network models to easily compare network properties such as connectivity, pore size distribution and network complexity using 3D μ CT data was shown. This use of pore network models for cultural heritage applications is a novel application of these models, which were originally developed from a reservoir engineering perspective.

References

- S. Brown and M. Smith. A transient-flow syringe air permeameter. *Geophysics*, 78(5):D307–D313, sep 2013. ISSN 0016-8033. doi: 10.1190/geo2012-0534.1.
- T. Bultreys, L. Van Hoorebeke, and V. Cnudde. Multi-scale, micro-computed tomography-based pore network models to simulate drainage in heterogeneous rocks. *Advances in Water Resources*, 78:36–49, apr 2015. ISSN 03091708. doi: 10.1016/j.advwatres.2015.02.003.
- V. Cnudde. *Exploring the potential of X-ray tomography as a new non-destructive research tool in conservation studies of natural building stones*. PhD thesis, Ghent University, 2005.
- V. Cnudde, J. Dewanckele, M. A. Boone, M. N. Boone, T. De Kock, L. Brabant, M. Duser, M. de Ceukelaire, H. de Clercq, R. Hayen, and P.J.S. Jacobs. High-Resolution X-Ray CT for 3D Petrography of Ferruginous Sandstone for an Investigation of Building Stone Decay. *Microscopy Research and Technique*, 74(11):1006–1017, 2011. doi: 10.1002/jemt.20987.
- W. De Boever, H. Derluyn, D. Van Loo, L. Van Hoorebeke, and V. Cnudde. Data-fusion of high resolution X-ray CT, SEM and EDS for 3D and pseudo-3D chemical and structural characterization of sandstone. *Micron*, apr 2015. ISSN 09684328. doi: 10.1016/j.micron.2015.04.003.
- J. Dewanckele, T. De Kock, G. Fronteau, H. Derluyn, P. Vontobel, M. Dierick, L. Van Hoorebeke, P. Jacobs, and V. Cnudde. Neutron radiography and X-ray computed tomography for quantifying weathering and water uptake processes inside porous limestone used as building material. *Materials Characterization*, 88:86–99, feb 2014. ISSN 10445803. doi: 10.1016/j.matchar.2013.12.007.
- H. Dong and M. J. Blunt. Pore-network extraction from micro-

- computerized-tomography images. *PHYSICAL REVIEW E*, 80(036307), 2009.
- C. Hall and W. D. Hoff. *Water transport in brick, stone and concrete*. Spon Press, 2002. ISBN 0-419-22890-X.
- P. Hudec. Durability of Rock as Function of Grain Size, Pore Size, and Rate of Capillary Absorption of Water. *Journal of Materials in Civil Engineering*, 1(1):3–9, 1989.
- M. Huysmans, L. Peeters, G. Moermans, and A. Dassargues. Relating small-scale sedimentary structures and permeability in a cross-bedded aquifer. *Journal of Hydrology*, 361(1-2):41–51, oct 2008. ISSN 00221694. doi: 10.1016/j.jhydrol.2008.07.047.
- M. a. Ioannidis, M. J. Kwiecien, and I. Chatzis. Statistical analysis of the porous microstructure as a method for estimating reservoir permeability. *Journal of Petroleum Science and Engineering*, 16(4):251–261, 1996. ISSN 09204105. doi: 10.1016/S0920-4105(96)00044-7.
- M. Karoglou, A. Moropoulou, A. Giakoumaki, and M. K. Krokida. Capillary rise kinetics of some building materials. *Journal of colloid and interface science*, 284(1):260–4, apr 2005. ISSN 0021-9797. doi: 10.1016/j.jcis.2004.09.065.
- E.W. Llewellyn. LBflow: An extensible lattice Boltzmann framework for the simulation of geophysical flows. Part I: theory and implementation. *Computers & Geosciences*, 36(2):115–122, feb 2010. ISSN 00983004. doi: 10.1016/j.cageo.2009.08.004.
- P.N. Manoudis, A. Tsakalof, I. Karapanagiotis, I. Zuburtikudis, and C. Panayiotou. Fabrication of super-hydrophobic surfaces for enhanced stone protection. *Surface and Coatings Technology*, 203(10-11):1322–1328, feb 2009. ISSN 02578972. doi: 10.1016/j.surfcoat.2008.10.041.
- P. Mostaghimi, M. J. Blunt, and B. Bijeljic. Computations of Absolute Permeability on Micro-CT Images. *Mathematical Geosciences*, 45(1): 103–125, 2013. ISSN 18748961. doi: 10.1007/s11004-012-9431-4.
- T. G. Nijland, C. W. Dubelaar, R. P. J. van Hees, and T. J. M. van der Linden. Black weathering of Bentheim and Obernkirchen sandstone. *Heron*, 48 (3):179–195, 2003.
- R. Peruzzi, T. Poli, and L. Toniolo. The experimental test for the evaluation

- of protective treatments: a critical survey of the capillary absorption index. *Journal of Cultural Heritage*, 4(3):251–254, jul 2003. ISSN 12962074. doi: 10.1016/S1296-2074(03)00050-5.
- T Ramstad, P-E Øren, and S Bakke. Simulation of two-phase flow in reservoir rocks using a lattice-Boltzmann method. Technical report, 2009.
- O. Rozenbaum and S. Rolland Du Roscoat. Representative elementary volume assessment of three-dimensional x-ray microtomography images of heterogeneous materials: Application to limestones. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics*, 89(5):1–11, 2014. ISSN 15502376. doi: 10.1103/PhysRevE.89.053304.
- A. Tsakalof, P. Manoudis, I. Karapanagiotis, I. Chrysoulakis, and C. Panayiotou. Assessment of synthetic polymeric coatings for the protection and preservation of stone monuments. *Journal of Cultural Heritage*, 8(1):69–72, jan 2007. ISSN 12962074. doi: 10.1016/j.culher.2006.06.007.

7

Preliminary results of the direct combination of μ CT and XRF on sandstone

In this chapter we show the first experiments using the new Herakles setup developed by UGCT / XMI (X-ray Microspectroscopy and Imaging), which is designed to combine high resolution CT with XRF measurements. These results explain the principle of the Herakles setup and show that this technique is extremely promising for future research applications. The completion of this system will be the next step in combining structural and chemical information at high resolutions, and thus in the research field of this thesis.

7.1 Introduction

7.1.1 X-ray fluorescence

X-ray fluorescence or XRF is an analytical method used to determine the elemental composition of samples under investigation. In XRF, the sample is irradiated with an X-ray beam. As these X-ray photons interact with electrons orbiting an atom core, these electrons can be ejected from the atom. This can cause a vacancy in an inner electron shell of the atom, which will be filled with an electron coming from an electron shell further away from the core. During this fall-back, the electron releases energy in the form of an X-ray photon with an energy equal to the energy difference between the orbitals involved in this process. The energy of the X-rays that are emitted by a certain element is characteristic for this specific element, hence the name characteristic radiation. Analysis of the spectrum of X-rays that is emitted by a sample can therefore be used to determine the exact elemental composition of this sample. The energy of the characteristic X-rays is of course always lower than the primary X-ray beam energy used to excite the sample, and the fluorescent radiation of light elements is of low energy. Due to this low energy, the characteristic photons of elements with an atomic number below 13 (Al) are absorbed to a large extent, even by the surrounding air and the beryllium window covering the detector. To enhance the range of detectable elements, vacuum conditions can be used, together with polymer windows. The lightest element that can be thus analysed in practice is usually around Na ($Z = 11$); lighter elements have a very low fluorescence yield. As in SEM-EDS, the characteristic X-ray photons are also analysed using energy-dispersive spectroscopy, recording the entire energy spectrum, produced by all detectable elements at the same time.

7.1.2 The Herakles system

The μ CT components of the Herakles systems were already introduced in chapter 2, but the implementation of an XRF system on the same setup, that is linked to the CT part makes this setup unique (figure 7.1). In past experiments, a direct correlation between μ CT and XRF on the same system could only be achieved by combining lab-based CT with synchrotron XRF (De Samber et al., 2008) or by performing all

measurements at synchrotron facilities. Herakles is equipped with two XRF measurement stations with two silicon drift detectors each, produced by SGX, with a crystal surface of 100 mm^2 and a crystal thickness of $750 \text{ }\mu\text{m}$. At the first XRF station, confocal measurements will be possible, since one of the detectors will be equipped with the necessary optics to focus on an exact location in the sample (De Jonge and Vogt, 2010). The second XRF station is designed to perform XRF tomography (Silversmit et al., 2009). In this case, line profiles of the sample are acquired at different angles over a total interval of 180° , enabling reconstruction of the elemental composition of a slice in the material. The system is still under development, making the results described below preliminary and incomplete, as improvements still need to be made in terms of hardware and software for both the acquisition and analysis of data and control of the hardware. Herakles was built in the framework of project AUGÉ/11/025, funded by the Hercules Foundation (www.herculesstichting.be).

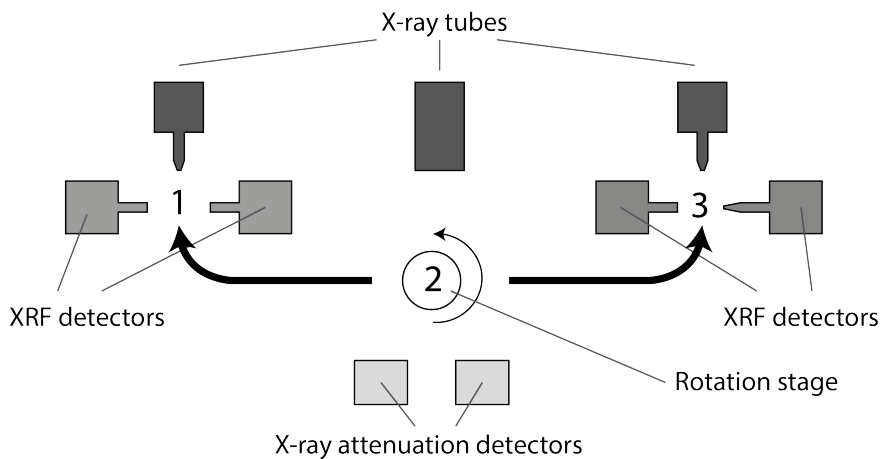


Figure 7.1: Schematic representation of the Herakles setup. Position 1 is used for XRF tomography, position 2 for X-ray attenuation tomography and position 3 for confocal XRF measurements. One of the XRF detectors at position 3 is equipped with focusing optics to enable confocal acquisition. The entire rotation stage can move between the three positions.

7.2 Preliminary results

7.2.1 XRF mapping based on X-ray CT data

A first experiment was the combination of a full tomographam with an XRF map of the analysed sample. Similar experiments have been conducted before by using micro-XRF and μ CT at separate systems (Cnudde et al., 2009; Boone et al., 2011). In this experiment, a 1 mm cylindrical Vosges sandstone sample was scanned using the μ CT part of Heracles, and based on the projection data an interesting zone for XRF can be selected. The ultimate goal will be to select points of interest for XRF analysis directly from complete reconstructed 3D volumes. The Vosges sandstone sample was scanned in a helical configuration, as the RadEye 1 detector is only capable of imaging in 'landscape' mode, which would result in a scan of a very limited region of the sample. A voxel size of 1.4 μ m was reached in this configuration, enabling clear grain and porosity identification. Based on the first projection of the μ CT scan, an interesting area for XRF mapping was selected (figure 7.2 A), with a size of 0.9 mm width and 1.4 mm in height. A mapping was performed across this volume, by taking a full XRF spectrum every 10 μ m, and each point was analysed during 5 seconds live time. The acquisition was performed two-dimensional, and did not take the curvature of the cylindrical sample into account, an issue that will be resolved in the future by taking confocal measurements of the exact pixels at the edge of the sample. Therefore, measurement is restricted to a small area close to the centre of the sample at this point, as fluorescent X-rays that are further away do not hit the XRF detector. Furthermore, mapping the sample in such a way does not give any idea on the depth of certain elements in the sample. Although light elements will not emit any signal if they lay deeper than a couple of tens of μ m below the surface, heavy elements such as iron and titanium will produce an XRF signal as deep as a couple of hundreds of μ m.

Although the full XRF spectrum is analysed at each point, the user can select the areas of the spectrum corresponding to specific minerals, in order to do sample analysis. In figure 7.2, maps for iron, titanium and potassium are shown. As can be seen, the titanium-rich areas correspond to two different dense grains that are visible in the projection. Iron-distribution is again not uniform throughout the sample, even in a small area as the one that is imaged. Areas high in potassium indicate clay

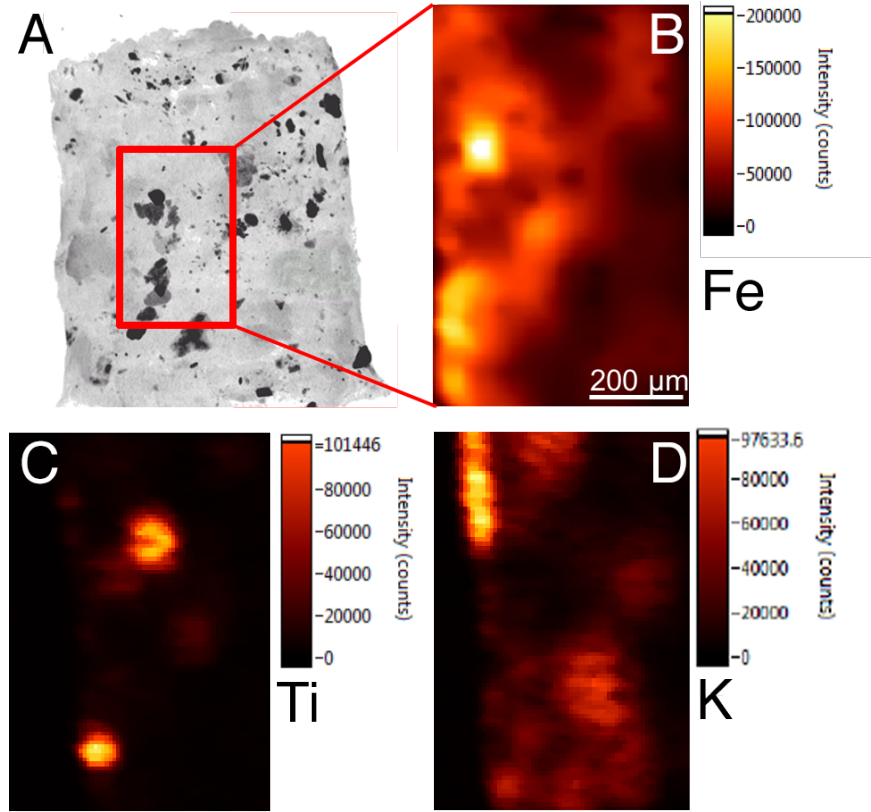


Figure 7.2: Maximum intensity projection render of the analysed Vosges sandstone sample 70 kv, 3W and 1.5 μm resolution (A), with XRF maps for Fe (B), Ti (C) and K (D), acquired at 40 kV, 40 W, 5 s lifetime and 10 μm resolution.

minerals or feldspars. Although figure 7.2 clearly shows the potential of future applications using Herakles, it also reveals the challenges that should be overcome, such as a correct correlation between the XRF maps and the CT scan.

7.2.2 XRF linescan of sample edge over full rotation

In the case of an XRF linescan at the sample surface, the sample was rotated and at fixed radial intervals the spectrum was measured. In this case, this interval was 20° , resulting in 18 analysis points over one rotation. During this measurement, the beam operated at 40 kV with a

beam current of 0.1 mA. Each point was measured during a lifetime of 60 seconds. The angular interval was kept quite big since measurements had to be performed manually, but future work on the system will allow automatic acquisition of this circle and even link it to a certain reconstructed slice. Therefore, in the future, the real limit in the number of points will be the resolution at which the XRF points can be measured. Like in the previous example, the spectrum that was measured originated from the bulk of the sample, therefore also sub-surface particles were measured, in which heavy elements are more easily detected than lighter ones. The line distributions that were obtained for K and Fe show variation between low and higher values, indicating areas where different grains of clay or feldspar for potassium and iron oxides in the case of iron are hit. Figure 7.3 shows there is a negative correlation between Si and K, and high concentrations of Fe and Ti occur in the same points, a phenomenon that was also visible in the XRF maps of the previous section.

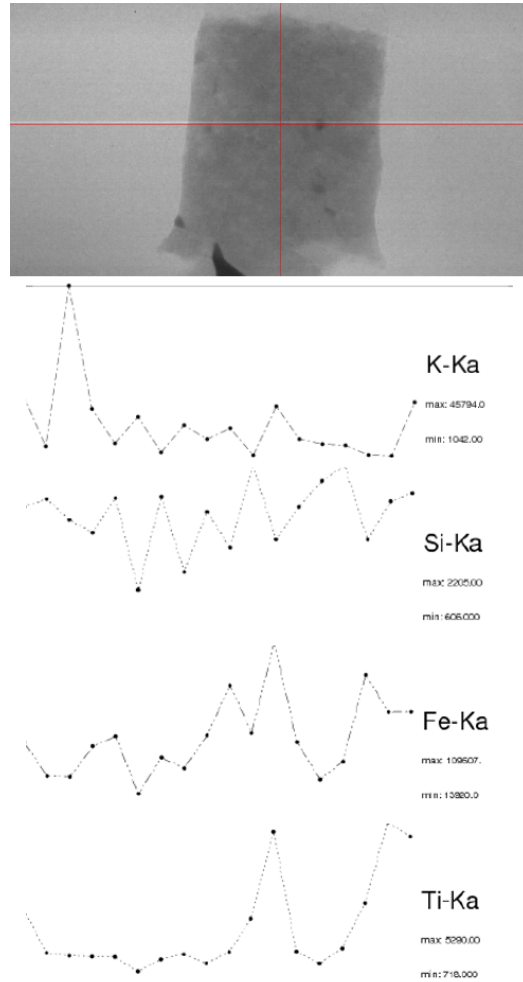


Figure 7.3: Linescans over a full rotation for K, Si, Fe and Ti. The first point is always the place of the cross in the X-ray projection. The sample is 1 mm in diameter.

7.2.3 Bulk chemical analysis of a glauconite grain

A last measurement was performed on a glauconite grain of around 300 μm that was measured on a stick. Again, first a high resolution tomographic scan was performed, to check if there was any obvious morphological variation in the sample. Since this was not the case, four random points in the volume for total XRF analysis were selected, so that

an average spectrum could be calculated. At each point, a lifetime of 120 seconds was measured using a beam voltage of 40 kV and a current of 0.1 mA. The summation of the different measurements only served to improve the statistics of the data, as all four measurements resulted in exactly the same spectrum. Using this method, the elemental composition of an unknown sample can be identified, or in other cases the elemental composition of different phases inside the same sample. In the case of this glauconite grain, many different elements were detected, as can be seen in figure 7.4. The peak for argon is coming from the air, as air contains a significant amount of Ar (0.9%).

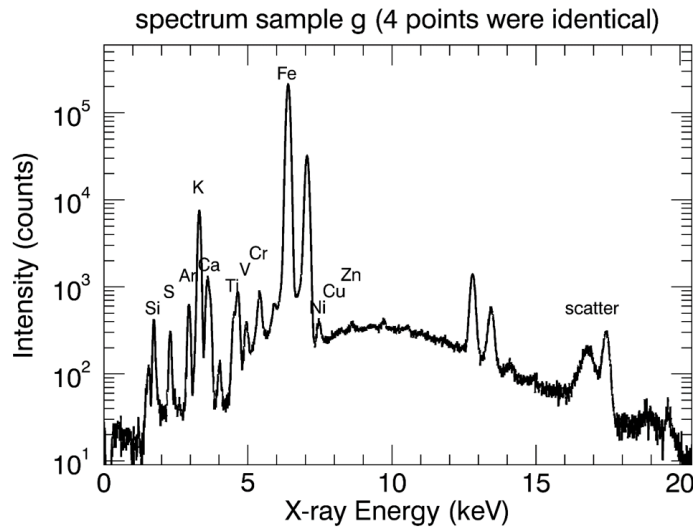


Figure 7.4: Full XRF spectrum of the analysed glauconite grain.

7.3 Further development

A major development of Herakles will be the ability of confocal XRF acquisition, enabling users to select an exact point in space to perform an XRF measurement on. Herakles will have the unique possibility to directly select these points based on a reconstructed CT volume. This principle is explained in figure 7.5: by selecting a point on a 2D slice through the volume (figure 7.5, left), the acquisition software can read out the exact x, y and z coordinates of this point. The software will then check

the orientation of the X-ray beams entering and exiting the sample, and ensure there is not a part of the sample or the hardware preventing good acquisition (figure 7.5, right).

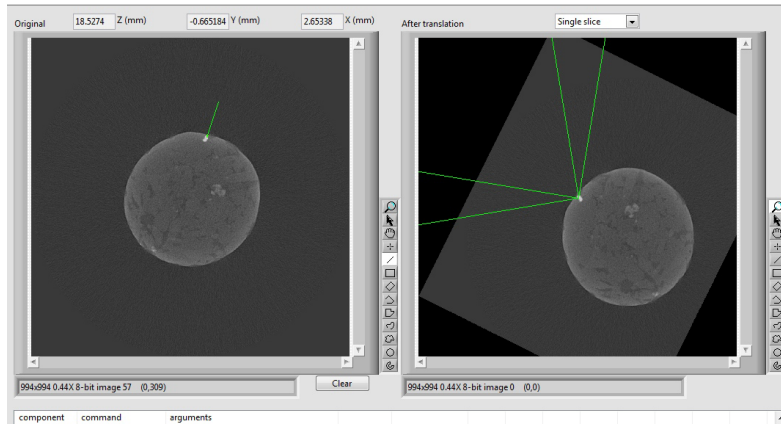


Figure 7.5: Screenshot of the acquisition software for confocal XRF. Left: selection of a point on a 2D slice through the reconstructed volume. Right: Display of the X-ray beam entering and exiting the sample, to verify if nothing is preventing acquisition.

In this step, a threshold value can also be chosen to separate the sample from the surrounding air, enabling the software to calculate the exact trajectory that can be followed to measure the XRF spectrum of the entire outer edge of the visualised CT slice. When the imaged sample is a lighter material than stone, this same software can be used to set up a horizontal grid of points, to map a region in the same plane as the CT slice. However, the high attenuation coefficient of stone prohibits this measurement, as all of the created characteristic X-rays would be self-adsorbed by the sample. Furthermore, development of the second XRF station of Herakles will enable scanning-probe XRF tomography, a setup that provides full 2D XRF reconstructions of a single slice through a sample (Silversmit et al., 2009). Although this measurement is more efficient than confocal acquisition of a grid of points, these experiments generally take many hours to complete, a problem that will be reduced by using two XRF detectors.

References

- M Boone, J Dewanckele, V Cnudde, G Silversmit, E Van Ranst, P Jacobs, L Vincze, and L Van Hoorebeke. Three-dimensional phase separation and identification in granite. *Geosphere*, 7(1):79–86, 2011. doi: 10.1130/ges00562.1.
- V. Cnudde, G. Silversmit, M.N. Boone, J. Dewanckele, B. De Samber, T. Schoonjans, D. Van Loo, Y. De Witte, M. Elburg, L. Vincze, V H Luc, J Patric, V Cnudde, G Silversmit, M Boone, J Dewanckele, B De Samber, T Schoonjans, D Van Loo, Y De Witte, M Elburg, L Vincze, L Van Hoorebeke, and P Jacobs. Multi-disciplinary characterisation of a sandstone surface crust. *Science of the Total Environment*, 407(20): 5417–5427, 2009. doi: 10.1016/j.scitotenv.2009.06.040.
- Martin D. De Jonge and Stefan Vogt. Hard X-ray fluorescence tomography—an emerging tool for structural visualization. *Current Opinion in Structural Biology*, 20(5):606–614, 2010. ISSN 0959440X. doi: 10.1016/j.sbi.2010.09.002.
- B. De Samber, R. Evens, K. De Schamphelaere, G. Silversmit, B. Masschaele, T. Schoonjans, B. Vekemans, C. R. Janssen, L. Van Hoorebeke, I. Szalóki, F. Vanhaecke, G. Falkenberg, and L. Vincze. A combination of synchrotron and laboratory X-ray techniques for studying tissue-specific trace level metal distributions in *Daphnia magna*. *Journal of Analytical Atomic Spectrometry*, 23(6):829, 2008. ISSN 0267-9477. doi: 10.1039/b800343m.
- G. Silversmit, B. Vekemans, F. E. Brenker, S. Schmitz, M. Burghammer, C. Riekkel, and L. Vincze. X-ray fluorescence nanotomography on cometary matter from comet 81P/Wild2 returned by stardust. *Analytical Chemistry*, 81(15):6107–6112, 2009. ISSN 00032700. doi: 10.1021/ac900507x.

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Conclusions and future outlook

The main research subject in this work was to study the internal structure and composition of natural stones across different length scales, going from nanometre to centimetre scale. In order to do so, quantitative image-based analysis methods were used, going from very traditional geological microscopy methods to highly innovating, synchrotron-based analysis methods. The importance of this characterisation and the multi-scale nature of natural stones is elaborately discussed in the introduction of this thesis. In this introduction is it obvious that focusing only on the pore scale of rocks is not a limitation, and that even this pore space already spans 8 orders of magnitude. Chapter 1 explains in high detail the traditional geological research methods of optical microscopy and scanning electron microscopy. These methods have been used for many decades and have become basic analysis techniques, taught to students, and mastered by many geologists. Nevertheless, literature shows that even these methods are used for high-end, innovating research and they have by no means become obsolete. In the same chapter, the main materials that were used for the research in this thesis were introduced. The choice was made to perform most of the work on sandstones, as they tend to have a less complex and therefore easier to image structure than many limestones. Three different sandstones were chosen, each with their

own characteristics. The German Bentheim sandstone is a frequently used analog for reservoir rock in fluid flow modelling, but also a wide-spread building stone in Belgium, The Netherlands and Germany. The stone was selected for this research, as in many others, for its simple structure and low chemical complexity. As the material is little more than a stacking of quartz grains with very little pore-filling minerals and cement, it is an excellent stone for first applications of a certain method. The Vosges sandstone is a material that is clearly more complex, both in terms of pore space and mineralogy. The material is much more fine-grained, resulting in smaller pores, and contains a significant amount of clay minerals and weathered feldspars, filling the pores and changing its flow characteristics. This makes the stone perfect for methodological studies involving multi-scale analysis and multi-technique analysis of the pore space and mineralogical components. Kandla Grey is the third sandstone, and has a very low porosity, unlike Bentheim and Vosges sandstones. This Indian sandstone consists almost entirely of quartz, but the low amount of clay minerals cause troubles in the use and durability of this stone. Not many techniques exist for characterisation of the tiniest pores in this sandstone, especially not in three dimensions.

An extensive review of μ CT, phase-contrast CT, FIB-nanotomography and ptychographic tomography provided the current state of the art for these 3D material analysis techniques. In particular, these methods were chosen since they that provide images with high spatial resolutions. Focused ion beam nanotomography (FIB-nt) and ptychographic tomography provide both 3D structural information at resolutions in the order of several tens of nanometre. Although FIB-nt is growing fast, both methods are still new and non-standard in geosciences. Ptychographic tomography is a method with high potential in geosciences, especially in samples where very small features are important. All of the methods described have their own strengths and weaknesses, and not a single method is usually suited for a full analysis of natural stone. Although μ CT is very versatile and allows for multi-scale analysis across different sample sizes, the limited chemical information it provides remains a main drawback to the technique. Therefore, it is often combined with the traditional microscopy techniques, that do not provide 3D information but on the other hand offer mineralogical or chemical information. Furthermore, these techniques allow for analysis of samples at their maximum resolution, regardless of sample size, by mosaic imaging. Also at the highest spatial resolutions, μ CT hits its limits at around 100 to 500 nm. There it can take benefit in a

combination with high-resolution imaging methods like FIB-nt and ptychographic tomography. Ptychographic tomography even couples this high-resolution imaging to being non-destructive, enabling the analysis of samples under changing environmental conditions. A main down-side for these methods however is their inability to perform multi-scale investigations, as both methods are limited to the analysis of very small volumes, typically smaller than 100 μm . Both methods can provide a certain degree of chemical information. In ptychographic tomography this is in the form of 3D distributions of the electron density in a sample, whereas FIB-nt can be coupled to EDS analysis, sadly creating measurements that take in the order of days.

	3D	Non-destructive	Chemical information	Multi-scale analysis
Optical microscopy	x	x	✓	✓
SEM / EDS	x	✓	✓	✓
μCT	✓	✓	x	✓
FIB-nt	✓	x	✓	x
Ptychographic tomography	✓	✓	✓	x

Figure 8.1: Comprehensive overview of the methods described in this thesis and their possibility to perform 3D analysis, whether or not they are non-destructive, if they provide chemical information and have the ability to analyse multiple sample scales and spatial resolution.

8.1 Combination of different imaging methods

In this thesis, we were able to successfully combine different traditional and novel research technique, for an integrated chemical and structural characterisation of sandstones. Using data-fusion between μCT , electron microscopy and EDS, a relatively large volume $(1.5\text{ cm})^3$ of rock was analysed across different scales. In first attempts to characterise the Vosges sandstone using μCT , the limits of the technique were exposed. Although this method is excellent to gain structural information on a sample,

especially when using different sample sizes, the absence of true chemical information is a real disadvantage. In some cases, prior knowledge on a sample's chemical components can overcome this disadvantage. However, this approach requires both a good separation of individual grains, and a good contrast between the different minerals inside the rock.

When contrast between different mineral phases is low (e.g. between quartz, micas, clays and feldspars in the Vosges sandstone) or when some elements are not clearly present in individual grains or high concentrations (e.g. the iron-rich cement in the Vosges sandstone), a different research methodology had to be developed. Furthermore, when dealing with heterogeneous rocks with relatively small features, it is not always possible to fit the sample size to the resolution that is needed to fully catch a material's structure. In this work this was the case for the Vosges sandstone, where a sample size of 1 to 2 mm was needed for analysis of the pore network and grain size distribution of the rock. At this sample size, a resolution of 0.86 μm could be obtained, using UGCT's Medusa setup. Unfortunately, such a small sample size was inadequate to see local changes in density of the material or variations in the porosity. Therefore, μCT on a much larger sample of 1.5 mm, more representative for the material's composition, was needed, which evidently did not provide as much information on the rocks's microstructure. Using HECTOR, a voxel size of around 9 μm could be reached. In this volume, local variations in overall porosity or density could easily be observed, and it was shown that the distribution of dense inclusions was not homogeneously spread across the sample.

In chapter 4, a workflow to enhance the μCT data described above was suggested and executed. The combination of μCT at different resolutions and SEM imaging provided high-resolution 2D images over the entire surface area of the 1.5 mm CT sample. Using well-known, landmark-based registration algorithms, these 2D images could be aligned with the lower-resolution 3D dataset, providing additional information on the structure of the grains and pores of the sample. Using elemental mapping with EDS, information on the local occurrence of different mineral phases could be added, enabling to acquire a pseudo-3D distribution of the distribution of these phases. However, EDS mapping is not accurate enough to distinguish between different clay minerals and micas, or even between these groups and feldspars. The latter distinguish has to be made based on the morphological properties of the grains, as

micas and clays tend to be more fine-grained or elongated than feldspar grains.

The results of chapter 4 showed that inside the Vosges sandstone, layers with higher iron-concentrations are present, and since the iron-oxides in which this iron is present occur finely dispersed in the cement of the rock, they are not visible in the μ CT data of the large volume. Furthermore, the combination of a relatively low-resolution μ CT scan with higher-resolution SEM images allowed for the registration of a small microplug inside the larger sample. Without the intermediary information of the SEM images, matching locations between low- and high-resolution CT scans would not be traceable. In this case, the microplug appeared to be coming from a relatively high-porosity region of the Vosges sandstone.

8.2 High-resolution imaging of the clay fraction inside sandstones

A big challenge in this thesis was high-resolution imaging of the smallest grains and pores inside the studied sandstones. In order to image these very small elements, traditional μ CT does not reach the resolution required, and although SEM can be used to image the microstructure inside clay minerals and micas, these do not provide 3D information on e.g. the connectivity of the pore network. In order to image these features experiments were performed using FIB-nt, but more attempts should be made in getting the acquisition parameters right and using BSE imaging on the system.

In chapter 5 we have shown the possibilities of ptychographic tomography for non-destructive imaging of geomaterials at extreme resolutions. The resolutions that were obtained during measurements at the cSAXS beam line were before only acquired with FIB-nt, which involves total evaporation of the sample. Ptychographic tomography enables imaging of clay minerals and micas at a grain-size level, and the studying of their behaviour under different states of relative humidity. Furthermore, as ptychographic tomography provides quantitative 3D distributions of the electron density throughout the analysed volume, the different clay minerals and iron oxides present in these tiny samples could be identified and their spatial distribution could be analysed. Individual iron oxide particles coating larger grains could be distinguished, the same particles that give the Vosges sandstone its pink colour. Ptychographic tomography

showed potential for the imaging of fluids in micropores, which can provide a possible application for reservoir geology and hydrogeology.

8.3 Correlation between laboratory measurements of capillary absorption, permeability and image-based simulations

A next step in validating the work performed during this Ph.D. research, was validation of the obtained structural information in real-life applications. A common application of 3D structural data is the simulation of fluid flow through the segmented pore system of rocks. Although this application is mostly used to predict flow in oil and gas reservoirs or aquifers, in chapter 6 experiments and simulations were performed to gain understanding in laboratory measurements of the capillary absorption coefficient for cultural heritage applications. In this chapter, a correlation was made between measurements of the capillary absorption coefficient and in-situ measurements of the permeability using a portable air permeameter, on nine different rocks. In general, the results showed a positive trend between capillary absorption and the connectivity and porosity, as was to be expected from literature. μ CT scans were performed for each material, in order to gain insight in porosity, pore size distribution and connectivity of the pore network. These parameters were obtained by extracting pore network models from the 3D images, using a grain-based extraction method. Each sample was scanned using the same parameters, and the same extraction algorithm was used, to enable comparison between the different materials. Furthermore, the pore network parameters were used to provide information on the correlation between capillary absorption measurements and permeability measurements. Based on this results, there could be a to introduce on-site permeability measurements as a standard test for cultural heritage applications. Further work should be done in this field, validating the method on other granular and non-granular materials, with a large spread in capillary absorption rate and porosity. Furthermore, research should be done to check if the response of permeability to processes like stone consolidation or restoration is similar to that of the capillary absorption coefficient, to really enable large adaptation of the method in the cultural heritage world.

8.4 Outlook

Apart from the future work that could follow the individual chapters described above, huge progress is expected from the combination of nano-CT and high-resolution XRF, using the Herakles system of UGCT and XMI, of which preliminary results are shown in chapter 7. Using this system, direct correlation between structure and chemical composition can be made, without the complicated step of image registration or the need to move the sample. Although the first results and proof of principle are provided in chapter 7, the setup needs to be finished and the hardware and software need further optimisation and testing, before Herakles can be used as standard equipment. Perhaps the most important improvement in the near future will be the possibility of confocal imaging, allowing for exact measurement of the surface of a specimen or a certain area in the 3D volume. This way, similar results as the ones in chapter 4 will be possible, be it on smaller specimens and with very long acquisition times. Other possibilities for future research are into the production of samples in the order of around 25 to 50 μm . Although FIB/SEM is an excellent method for the production of samples up to around 10 μm , the production times are too high when sample size goes up. Getting this right is an absolute must for the further use of ptychographic tomography or ultra-high resolution X-ray tomography. Furthermore, the obtained 3D volumes at extreme resolutions should be incorporated in existing fields such as pore network modelling and direct fluid flow modelling. In PNM, high-resolution images should serve as input for the tiniest pores in the network, where so far mostly estimations have been used. Finally, further research should be performed on the linking of pore network characteristics and traditional laboratory tests on building stones, so that in the future, there might be a possibility to replace these tests by image-based analysis and simulations on a very limited amount of samples.

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Bibliography

A1 Publications

De Boever, W., Bultreys, T., Derluyn, H., Van Hoorebeke, L., Cnudde, V., (under review) Comparison between traditional laboratory tests, permeability measurements and CT-based fluid flow modelling for cultural heritage applications. SCIENCE OF THE TOTAL ENVIRONMENT

De Boever, W., Diaz, A., Derluyn, H., Van Stappen, J., De Kock, T., Dewanckele, J., Bultreys, T., Boone, M.N., De Schryver, T., Skjønshjell, E., Holler, M., Breiby, D., Cnudde, V. (2015). Characterization of composition and structure of clay minerals in sandstone with ptychographic X-ray tomography. APPLIED CLAY SCIENCE, 118, 258-264

De Boever, W., Derluyn, H., Van Loo, D., Van Hoorebeke, L., Cnudde, V. (2015) Data-fusion of high resolution X-ray CT, SEM and EDS for 3D and pseudo-3D chemical and structural characterisation of sandstone. MICRON, 74, 15-21

Cardenes, V., Merinero, R., **De Boever, W.**, Rubio-Ordóñez, A., Dewanckele, J., Cnudde, J-P., Boone, M.N., Van Hoorebeke, L., Cnudde,

V. (2015) Characterization of Micropyrte Populations in Low-Grade Metamorphic Slate: A Study Using High-Resolution X-Ray Tomography. PALAEOGEOGRAPHY PALAEOCLIMATOLOGY PALAEOECOLOGY, in press.

Isebaert, A., **De Boever, W.**, Descamps, F., Dils, J., Dumon, M., De Schutter, G., Van Ranst, E., Cnudde, V., Van Parys, L. (2015) Pore-related properties of natural hydraulic lime mortars: an experimental study. MATERIALS AND STRUCTURES, in press.

Cnudde, V., De Kock, T., Boone, M., **De Boever, W.**, Bultreys, T., Van Stappen, J., Vandevoorde, D., Dewanckele, J., Derluyn, H., Cardenes, V., Van Hoorebeke, L. (2015) Conservation studies of cultural heritage: X-ray imaging of dynamic processes in building materials. EUROPEAN JOURNAL OF MINERALOGY, 27(3): 269-278

De Kock, T., **De Boever, W.**, Dewanckele, J., Boone, M.A., Jacobs, P. and Cnudde, V. (2014). Characterization, performance and replacement stone compatibility of building stone in the 12th century tower of Dudzele (Belgium) ENGINEERING GEOLOGY, 184, 43-51

Dewanckele, J., Boone, M.A., De Kock, T., **De Boever, W.**, Brabant, L., Boone, M.N., Fronteau, G., Dils, J., Van Hoorebeke, L., Jacobs, P., Cnudde, V. (2013) Holistic approach of pre-existing flaws on the decay of two limestones. SCIENCE OF THE TOTAL ENVIRONMENT, 447, 403-414

Cnudde, V., **De Boever, W.**, Dewanckele, J., De Kock, T., Boone, M.A., Boone, M.N., Silversmit, G., Vincze, L., Van Ranst, E., Derluyn, H., Peetermans, S., Hovind, J., Modregger, P., Stampanoni, M., De Buysser, K., De Schutter, G. (2013) Multi-disciplinary characterization and monitoring of sandstone (Kandla Grey) under different external conditions. QUATERLY JOURNAL OF ENGINEERING GEOLOGY AND HYDROGEOLOGY, 46, 95-106

Book chapters

Cnudde, V., Dewanckele, J., De Boever, W., Brabant, L., De Kock, T. (2012) 3D characterization of grain size distributions in sandstone by means of X-ray computed tomography. QUANTITATIVE

MINERALOGY AND MICROANALYSIS OF SEDIMENTS AND
SEDIMENTARY ROCKS. in SHORT COURSE SERIES 42, 99-113

Conference proceedings

De Boever, W., Derluyn, H., Van Stappen, J., Dewanckele, J., Bultreys, T., Boone, M.N., De Schryver, T., De Kock, T., Skjonsfjell, E., Diaz, A., Holler, M., Cnudde, V. (2015) 3D imaging of clay minerals inside sandstone Pushing the spatial resolution limits using ptychographic tomography. ICTMS 2015, June 29th - July 3rd 2015 - Quebec City, Canada. *Presented as oral presentation by W. De Boever*

Cardenes, V., Cnudde, V., Merinero, R., Dewanckele, J., **De Boever, W.**, Cnudde, J.P. (2015) Determination of the REDOX paleoconditions: A High Resolution X-ray Tomography study of micro pyrite occurrence. ICTMS 2015, June 29th - July 3rd 2015 - Quebec City, Canada. *Presented as poster presentation by V. Cardenes.*

De Boever, W., Bultreys, T., Traska, M., Mock, A., Brabant, L., Cnudde, V. (2013) 3D Characterisation of the Bentheim sandstone and Euville limestone, in relation to fluid flow through their pore networks. PROCEEDINGS OF THE 14th EUROSEMINAR ON MICROSCOPY APPLIED TO BUILDING MATERIALS. *Presented as oral presentation by W. De Boever at EMABM 2013, June 12-15 2013, Helsingor, Denmark*

Cardenes Van Den Eynde, V., Cnudde, V., **De Boever, W.**, Mateos, F.J. (2013) Micro-CT and mercury intrusion porosimetry characterization of the fabric of roofing slate. ICTMS 2013, July 1-5 2013, Ghent, Belgium.

De Kock, T., Boone, M.A., Dewanckele, J., **De Boever, W.**, Vandevoorde, D., Boone, M.N., De Schutter, G., Lehmann, E., Jacobs, P., Cnudde, V. (2012) Monitoring frost susceptibility of limestone facies. 12th INTERNATIONAL CONFERENCE ON THE DETERIORATION AND CONSERVATION OF STONE, October 21-25 2012, New York City, USA. *Presented as oral presentation by T. De Kock.*

Conference contributions

De Boever, W., Cnudde, V., Derluyn, H., Bultreys, T., Boone, M.N., De Schryver, T., Van Stappen, J., Dewanckele, J., Van Loo, D. (2015) Multi-scale characterization of complex geomaterials using multiple imaging techniques. DIGITAL INDUSTRIAL RADIOLOGY AND COMPUTED TOMOGRAPHY, June 22-25, Ghent, Belgium. *Presented as oral presentation by W. De Boever.*

Bultreys, T., **De Boever, W.**, Van Hoorebeke, L., Cnudde, V. (2015) Multi-scale, image-based pore network models to simulate two-phase flow in heterogeneous rocks. 7th INTERNATIONAL CONFERENCE ON POROUS MEDIA, May 18-21 2015, Padua, Italy. *Presented as a poster by T. Bultreys*

De Boever, W., Derluyn, H., Bultreys, T., Van Hoorebeke, L., Cnudde, V. (2014) Data fusion of High Resolution X-ray CT and SEM/EDS for pseudo-3D elemental and structural characterization of the Vosges sandstone. 6th INTERNATIONAL CONFERENCE ON POROUS MEDIA, May 27-30, Milwaukee, USA. *Presented as oral presentation by W. De Boever*

Bultreys, T., **De Boever, W.**, Van Hoorebeke, L., Mehmani, A., Prodanovic, M., Cnudde, V. (2014) Image-based multi-scale pore network models to investigate two-phase flow in carbonate rocks. Shell Amsterdam Centennial conference. *Presented as oral presentation by T. Bultreys.*

Bultreys, T., Raeni, A.Q., **De Boever, W.**, Van Hoorebeke, L., Cnudde, V. (2014) Multi-scale, image-based pore network models to simulate two-phase flow in carbonate rocks. 6th INTERNATIONAL CONFERENCE ON POROUS MEDIA, May 27-30 2014, Milwaukee, USA. *Presented as oral presentation by T. Bultreys*

Bultreys, T., **De Boever, W.**, Brabant, L., Cnudde, V. (2013) Comparison of pore network models for the investigation of fluid flow properties in building stones. 5th INTERNATIONAL CONFERENCE ON POROUS MEDIA, May 21-24 2013, Prague, Czech Republic. *Presented as poster by T. Bultreys.*

De Boever, W., Cnudde, V., Dewanckele, J., Boone, M.A., De Kock, T., Boone, M.N., Van Ranst, E., Silversmit, G., Vincze, L., Derluyn, H., Peetermans, S., Hovind, J., Modregger, P., Stampanoni, M., De Buysser,

K., De Schutter, G. (2013) Characterisation of sandstone (Kandla Grey) weathering behaviour by frost and salt action. (2013) CRYSPOM III, Workshop on crystallization in porous media. *Presented as oral presentation by W. De Boever*

Dewanckele, J., **De Boever, W.**, De Kock, T., Boone, M.A., Boone, M.N., Brabant, L., Fronteau, G., Van Hoorebeke, L., Cnudde, V., Jacobs, P. (2012) Influence of limestone microstructure on gypsum crystallization. (2013) CRYSPOM III, Workshop on crystallization in porous media. *Presented as oral presentation by J. Dewanckele*

Claes, S., **De Boever, W.**, Bultreys, T., Brabant, L., Van Hoorebeke, L., Cnudde, V., Swennen, R. (2012) Multi-resolution CT for the quantification of reservoir properties in complex carbonate rocks. GEOLOGICA BELGICA 2012 *Presented as oral presentation by S. Claes.*

De Kock, T., Dewanckele, J., Boone, M.A., **De Boever, W.**, De Schutter, G., Jacobs, P., Cnudde, V. (2012) Wanted: suitable replacement stones for the Lede stone (Belgium). GEOPHYSICAL RESEARCH ABSTRACTS 14 *Presented as poster by T. De Kock at EGU 2012, Vienna.*

De Kock, T., Vandevoorde, D., Boone, M.A., Dewanckele, J., **De Boever, W.**, Lanzon, M., De Schutter, G., Van Hoorebeke, L., Jacobs, P., Cnudde, V. (2012) Compatibility study and adaptation of stone repair mortars for the lede stone (Belgium). GEOPHYSICAL RESEARCH ABSTRACTS 14 *Presented as oral presentation by T. De Kock at EGU 2012, Vienna.*

Goossens, M., De Kock, T., Dewanckele, J., Boone, M.A., **De Boever, W.**, Brabant, L., Louwye, S., De Ceukelaire, M., Vanhaecke, F., Cnudde, V. (2012) Characterization of fieldstone for a provenance study of local building stones and artifacts. *Presented as poster by M. Goossens at EGU 2012, Vienna.*

De Boever, W., Cnudde, V., Dewanckele, J., Boone, M.A., De Kock, T., Boone, M.N., Van Ranst, E., Silversmit, G., Vincze, L., Derluyn, H., Peetermans, S., Hovind, J., Modregger, P., Stampanoni, M., De Buysser, K., De Schutter, G. (2012) Durability of the Indian Kandla Grey sandstone under Western European climatic conditions. *Presented as poster by T. De Kock at EGU 2012, Vienna.*

Miscellaneous

Bultreys, T., **De Boever, W.**, Cnudde, V. (2014) 3D pore characterization and pore-scale transport modelling in earth sciences: an IFPRI review.

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List of abbreviations

- μ CT- micro-computed tomography
- XRD - X-ray diffraction
- NAPL - Non-aqueous polluting liquid
- PNM - Pore network model
- SEM - Scanning electron microscopy
- EDS - Energy-dispersive spectroscopy
- FIB-nt - Focused ion beam nanotomography
- BSE - Backscattered electron
- keV - Kilo-electronvolt
- FLM - Fluorescence light microscopy
- XPL - Cross-polarised light
- PPL - Planar polarised light
- REV - Representative elementary volume

- R.H. - Relative humidity (in %)
- Gy - Gray (unit of ionising radiation)