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4-DIMENSIONAL STUDIES OF FLUID-ROCK INTERACTION

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Abstract

Successful management of hydrocarbon reservoirs, geothermal energy extraction sites, radioactive waste and CO₂ storage sites depends on a detailed knowledge of fluid transport properties, porosity and permeability. Amongst deformation processes, fluid-rock interaction plays an important role in controlling the petrophysical properties of a rock. The presence of fluids in the rocks induce chemical and physical changes in compositions and texture, affecting porosity and permeability, hence influencing dynamic transport properties and fluid flow. Fluid-rock interaction processes have been deeply investigated in nature and in numerous experimental and numerical modelling studies. However, these studies lack a spatio-temporal characterization of the dynamic evolution of porosity and reaction microfabrics. There is no clear understanding of the spatio-temporal evolution of these properties in three dimensions, and how this evolution affects fluid percolation in the rock. Computed X-ray micro-Tomography (µCT) was applied to investigate these processes in three dimensions and observe their evolution in time (4DµCT). The combination of µCT with 2D analytical techniques (e.g. scanning electron microscope, SEM, electron microprobe, EMPA, electron backscatter diffraction, EBSD) furthermore enables the extrapolation of the information gained from 2D analyses to the 3rd and 4th dimension (4D µCT).

The thesis investigates two different categories of fluid-rock interaction processes, by using 4DµCT to monitor the evolution of mineral reactions (in the first case) and porosity (second case) in relation to strain and time. In the first case study, natural rock samples were analysed. The samples show a compositional change along a strain gradient from olivinic metagabbros to omphacite-garnet bearing eclogites in a ductile shear zone. Synchrotron-based x-ray microtomography (sµCT) was applied to document the 3D evolution of garnets along the strain gradient (which represent the 4th dimension). The 3D spatial arrangement of garnet microfabrics can help determine the deformation history and the extent of fluid-rock interaction active during deformation. Results from the sµCT show that in the low strain domain, garnets form a large and well interconnected cluster that develops throughout the entire sample and garnet coronas never completely encapsulate olivine grains. In the most highly deformed eclogites, the oblate shapes of garnets reflect a deformational origin of the microfabrics. EBSD analyses reveal that garnets do not show evidence
for crystal plasticity, but rather they highlight evidence for minor fracturing, neo-
nucleation and overgrowth, which points to a mechanical disintegration of the garnet
 coronas during strain localisation.

In the second case study, pressure-solution processes were investigated using
NaCl as rock-analogue, to monitor the evolution of porosity and pore connectivity in
four dimensions, providing a time-resolved characterization of the processes. NaCl
samples were uniaxially compacted and μCT scans were taken at regular interval
times to characterize the evolution of grain morphologies, pore space and macro-
connectivity of the samples. Different uniaxial loads, as well as different bulk sample
compositions (phyllosilicates and/or glass beads) were used to investigate their effect
on the process. Greater uniaxial loads, and the presence of phyllosilicates within
the deforming NaCl columns were found to enhance pressure-solution processes.
The pore space becomes highly disconnected in the presence of phyllosilicates, with
important implications for fluid percolation and dynamic transport properties. Mean
strain rates, calculated from volumetric Digital Image Correlation (3D-DIC) analyses,
were found to be higher where phyllosilicates were located. The combination of μCT
with volumetric DIC and SEM imaging proved to be an efficient analytical method
for investigating the dynamic behaviour of porosity and permeability during ongoing
pressure-solution processes.

The results showed that fluid-rock interaction critically modifies the rocks at the
pore/grain scale, with important consequences on dynamic fluid transport properties.
The combination of μCT with classical 2D techniques provided a better understanding
on the dynamic evolution of transport properties and fluid percolation during fluid-
rock interaction processes, allowing the characterization in three dimensions of
reaction microfabrics and porosity.
Lay summary

Within the Earth, fluids continuously interact with rocks, from the surface down to the deep mantle. When fluids interact with rocks, they modify the structure of the rock at the micro-scale, in terms of texture and composition. The open space between grains (porosity), which can be filled by air or fluids, will be modified too, which in turn affects how fluids can travel within the rocks. However, most investigations of rocks require destructive techniques, in which the samples are analysed in two dimensions, thereby missing information on the third dimension. These techniques are therefore limiting the analysis to one plane, and they do not allow to study the evolution of the process while it is happening. The use of Computed X-ray Microtomography (µCT) enables scientists to monitor the evolution of porosity and rocks microstructures with non-destructive testing of the rock. The samples are scanned with x-rays using the same protocols of medical CT scanning. Pictures are acquired at incremental angular intervals and a 3D dataset is reconstructed at the end, which allows investigation of the 3D internal structure of the sample. The technique was applied to two case-studies of fluid-rock interaction. In the first one, natural rock-samples, which show a compositional evolution due to deformation and fluid infiltration, were investigated along a deformation gradient. The technique allowed the collection of qualitative and quantitative information about the 3D evolution of the minerals (in particular garnet) in the rock with increasing deformation, which represents the 4th dimension. With increasing deformation, garnet volume increased, and the spatial distribution of garnet grains evolved from baseball-gloved shaped structures to elongated and sheared garnet aggregates due to the deformation. In the second case, an experiment was carried to monitor the evolution of porosity during pressure-solution creep (PSC). PSC is a process, in which material is dissolved, transported and re-precipitated elsewhere in the rock following a stress gradient. In these experiments, the evolution of porosity was monitored in three dimensions and over time, thereby yielding a 4D dataset. The process induces a great reduction in bulk porosity and pore connectivity, which strongly affects fluid percolation and transport properties within the rocks. The results show the capability of µCT to analyse geological processes at the micro-scale in four dimensions, without destructive testing of the rock.
Author’s Declaration

I declare that this thesis has been composed solely by myself and that it has not been submitted, either in whole or in part, in any previous application for a degree. Except where otherwise acknowledged, the work presented is entirely my own.

Alice Macente
2017
Acknowledgments

Now that I approached the end of this three and a half years long journey, I realised how incredible and amazing it has been. I grew not only as researcher, but as a person too, and many persons contributed to this. Along the way I met many extraordinary people, who will be in my life for many years ahead.

First at all, I would like to thank both my supervisors. They shaped me into the young researcher I am today, they showed me support and trust endless times and they both treated me as a collaborator rather than a subordinate. I am very grateful to both of them, for never letting me down and never letting me give up. The experiences at the synchrotron equipped me with an incomparable scientific and methodological background and I am very thankful for the opportunity. I thank Florian for his support during countless moments of the PhD and for challenging me when I needed to be pushed. I thank you for all the moments we shared in the lab, in many fieldtrips and during Structural Geology course: I learnt a lot from those experiences. I thank you for the opportunities I had in talking to many researchers through the EPS seminars, and for all the networking you encouraged me to do. Seeing your happiness after the EGU talks has been the most satisfying feeling of my work. I would like to thank Ian for his endless patience in the lab, and his countless useful suggestions in the image analysis process and not only. His help during the data acquisition and processing in the in-house CT scanner were highly appreciated. I would like to thank him for every time he spent few minutes of his time and kind words towards me whenever I needed to be reassured about data challenges. I also feel I should thank him for the huge amount of coffee I used to drink while performing image analysis on the microtomographic datasets. I thank you both, for the support and encouragement shown to me, when I mostly needed it. Since the very beginning, I felt part of a family rather than a group, and I could not have asked for more.

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Contents

Abstract i
Lay summary iii
Author’s Declaration iv
Acknowledgments vi
Table of Contents ix
List of Figures xiii
List of Tables xvi
List of Abbreviations xix

1 Introduction 1
  1.1 Natural and experimental fluid-rock interaction 2
    1.1.1 Fluid-rock interaction in nature 2
    1.1.2 2D laboratory investigations of fluid-rock interaction 4
    1.1.3 4D characterization of fluid-rock interactions 6
  1.2 Research motivations 8
  1.3 Thesis layout 10

2 Methods 13
  2.1 Introduction 14
  2.2 Computed X-ray microtomography 15
    2.2.1 A history of computed X-ray microtomography 15
    2.2.2 Principles of a µCT system 16
      2.2.2.1 µCT system 18
      2.2.2.2 Synchroton vs laboratory CT scanner apparatus 18
    2.2.3 Image correction and reconstruction 20
    2.2.4 Limitations of µCT systems 22
      2.2.4.1 Pre-reconstruction 22
      2.2.4.2 Post-reconstruction 23
    2.2.5 Image Analysis 24
  2.3 Digital Image Correlation: DIC 27
  2.4 Part I: Natural samples from Kråkeneset, Western Gneiss Region (Norway) 30
    2.4.1 Data acquisition 30
      2.4.1.1 Samples and samples preparation 30
      2.4.1.2 SµCT 30
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4.1.3 SEM/EDS/EPMA</td>
<td>32</td>
</tr>
<tr>
<td>2.4.1.4 EBSD</td>
<td>33</td>
</tr>
<tr>
<td>2.4.1.5 Quant3D</td>
<td>33</td>
</tr>
<tr>
<td>2.4.2 Data processing</td>
<td>34</td>
</tr>
<tr>
<td>2.4.2.1 SµCT data: reconstruction</td>
<td>35</td>
</tr>
<tr>
<td>2.4.2.2 SµCT data: filtering</td>
<td>35</td>
</tr>
<tr>
<td>2.4.2.3 SµCT data: segmentation</td>
<td>35</td>
</tr>
<tr>
<td>2.4.2.4 EBSD software</td>
<td>36</td>
</tr>
<tr>
<td>2.4.3 Data analyses</td>
<td>38</td>
</tr>
<tr>
<td>2.4.3.1 Garnet volume</td>
<td>38</td>
</tr>
<tr>
<td>2.4.3.2 Interconnectivity</td>
<td>39</td>
</tr>
<tr>
<td>2.4.3.3 Fabric and shape analysis: Quant3D</td>
<td>39</td>
</tr>
<tr>
<td>2.4.3.4 Data integration from multiple sources</td>
<td>40</td>
</tr>
<tr>
<td>2.5 Part II: Experimental deformation of NaCl</td>
<td>41</td>
</tr>
<tr>
<td>2.5.1 Experimental methods and data acquisition</td>
<td>41</td>
</tr>
<tr>
<td>2.5.1.1 Cell design</td>
<td>41</td>
</tr>
<tr>
<td>2.5.1.2 Sample preparation</td>
<td>43</td>
</tr>
<tr>
<td>2.5.1.3 Material test</td>
<td>43</td>
</tr>
<tr>
<td>2.5.1.4 Experimental setup</td>
<td>44</td>
</tr>
<tr>
<td>2.5.1.5 µCT scanning parameters</td>
<td>46</td>
</tr>
<tr>
<td>2.5.1.6 SEM</td>
<td>46</td>
</tr>
<tr>
<td>2.5.1.7 Volumetric Digital Image Correlation: 3D-DIC</td>
<td>46</td>
</tr>
<tr>
<td>2.5.2 Data processing</td>
<td>48</td>
</tr>
<tr>
<td>2.5.2.1 µCT data: filtering</td>
<td>48</td>
</tr>
<tr>
<td>2.5.2.2 µCT data: segmentation</td>
<td>49</td>
</tr>
<tr>
<td>2.5.2.3 µCT data: labelling</td>
<td>49</td>
</tr>
<tr>
<td>2.5.2.4 µCT data: separation</td>
<td>50</td>
</tr>
<tr>
<td>2.5.3 Data analyses</td>
<td>53</td>
</tr>
<tr>
<td>2.5.3.1 Vertical shortening</td>
<td>53</td>
</tr>
<tr>
<td>2.5.3.2 Bulk porosity</td>
<td>53</td>
</tr>
<tr>
<td>2.5.3.3 Pore size and shape</td>
<td>53</td>
</tr>
<tr>
<td>2.5.3.4 Interconnectivity</td>
<td>54</td>
</tr>
<tr>
<td>2.5.3.5 Strain analysis</td>
<td>55</td>
</tr>
<tr>
<td>2.5.3.6 Microstructural analysis</td>
<td>55</td>
</tr>
<tr>
<td>3 Strain-dependent spatial evolution of garnet grains</td>
<td>57</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>59</td>
</tr>
<tr>
<td>3.2 Geological Setting</td>
<td>61</td>
</tr>
<tr>
<td>3.3 Methods</td>
<td>63</td>
</tr>
<tr>
<td>3.4 Results</td>
<td>64</td>
</tr>
<tr>
<td>3.4.1 Petrographic characterization</td>
<td>64</td>
</tr>
<tr>
<td>3.4.2 Chemical compositions and mineral chemistry</td>
<td>67</td>
</tr>
<tr>
<td>3.4.3 4D spatial evolution of garnet grains</td>
<td>69</td>
</tr>
<tr>
<td>3.4.4 EBSD analysis: Misorientation of garnet grains in the shear zone</td>
<td>71</td>
</tr>
<tr>
<td>3.5 Discussion</td>
<td>76</td>
</tr>
<tr>
<td>3.5.1 Strain-dependent evolution of garnet microfabrics in the Kråkeneset shear zone</td>
<td>76</td>
</tr>
</tbody>
</table>
3.5.1.1 Where does all the garnet go? .............................. 76
3.5.1.2 What the morphological operator “Erosion” reveals about the garnet distribution .............................. 78
3.5.1.3 Micromechanisms involved ................................. 78
3.5.2 Implications for fluid flow, mass- and element transport .............................. 79
3.6 Conclusions .................................................. 82

4 Pressure-solution processes in NaCl .............................. 83

4.1 Introduction .................................................. 85
4.2 Theoretical background ....................................... 87
4.2.1 Thermodynamics and kinetics of PSC ........................ 87
4.2.1.1 The nature of the fluid interface .......................... 89
4.2.2 Experimental studies ....................................... 90
4.2.3 Stylolites .................................................. 94
4.2.4 Strain shadows and strain caps ................................ 96
4.3 Experimental procedure ....................................... 98
4.4 Results ...................................................... 100
4.4.1 Data description ........................................... 100
4.4.1.1 Pure NaCl ............................................. 100
4.4.2 NaCl-biotite/NaCl-kaolinite ................................ 105
4.4.3 NaCl-glass beads ......................................... 108
4.4.4 NaCl-glass beads-biotite .................................. 108
4.5 Results of digital image analysis .............................. 111
4.5.1 Bulk porosity .............................................. 111
4.5.1.1 Pure NaCl ............................................. 111
4.5.1.2 NaCl-biotite ......................................... 111
4.5.1.3 Porosity distribution and strain partitioning within the sample ............................................. 112
4.5.1.4 NaCl-glass beads ..................................... 115
4.5.1.5 NaCl-glass beads-biotite ................................ 115
4.5.2 Pore size and shape ........................................ 117
4.5.2.1 Pure NaCl ............................................. 117
4.5.2.2 NaCl-biotite ......................................... 117
4.5.2.3 NaCl-glass beads ..................................... 119
4.5.2.4 NaCl-biotite-glass beads .............................. 120
4.5.3 Interconnectivity ........................................... 125
4.5.4 Skeletonization of pore volumes ............................ 128
4.5.4.1 NaCl-biotite ......................................... 128
4.5.4.2 NaCl-biotite-glass beads .............................. 129
4.5.5 Strain analysis ............................................. 131
4.5.5.1 Pure NaCl ............................................. 131
4.5.5.2 NaCl-biotite ......................................... 134
4.5.5.3 NaCl-glass beads ..................................... 134
4.5.5.4 NaCl-glass beads-biotite .............................. 135
4.5.6 Microstructural analysis .................................... 139
4.5.6.1 Pure NaCl ............................................. 139
4.5.6.2 NaCl-biotite ......................................... 139
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5.6.3</td>
<td>NaCl-biotite-glass beads</td>
<td>139</td>
</tr>
<tr>
<td>4.6</td>
<td>Discussion</td>
<td>141</td>
</tr>
<tr>
<td>4.6.1</td>
<td>Mechanical and chemical processes during uniaxial compaction</td>
<td>141</td>
</tr>
<tr>
<td>4.6.1.1</td>
<td>Effect of uniaxial load</td>
<td>143</td>
</tr>
<tr>
<td>4.6.2</td>
<td>Pressure-solution in pure NaCl samples</td>
<td>144</td>
</tr>
<tr>
<td>4.6.3</td>
<td>Pressure-solution in the presence of phyllosilicates (e.g. biotite)</td>
<td>145</td>
</tr>
<tr>
<td>4.6.3.1</td>
<td>How does PSC occur in the presence of phyllosilicates?</td>
<td>145</td>
</tr>
<tr>
<td>4.6.4</td>
<td>Pressure-solution in the presence of glass beads</td>
<td>148</td>
</tr>
<tr>
<td>4.6.5</td>
<td>Pressure-solution in the presence of glass beads and biotite</td>
<td>149</td>
</tr>
<tr>
<td>4.6.6</td>
<td>Precipitation sites: overgrowth or neo-nucleation?</td>
<td>151</td>
</tr>
<tr>
<td>4.6.7</td>
<td>Effects of segmentation/separation algorithms</td>
<td>152</td>
</tr>
<tr>
<td>4.6.7.1</td>
<td>Cropping</td>
<td>154</td>
</tr>
<tr>
<td>4.6.8</td>
<td>Effects of size lower threshold at 10 or 125 cubic voxels</td>
<td>154</td>
</tr>
<tr>
<td>4.7</td>
<td>Summary</td>
<td>156</td>
</tr>
</tbody>
</table>

## 5 Final remarks

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Final discussions</td>
<td>160</td>
</tr>
<tr>
<td>5.1.1</td>
<td>Advances in fluid-rock interaction: what can µCT add to current investigation?</td>
<td>160</td>
</tr>
<tr>
<td>5.1.1.1</td>
<td>NaCl as rock-analogue material</td>
<td>162</td>
</tr>
<tr>
<td>5.1.2</td>
<td>Evaluation of µCT techniques and advances</td>
<td>164</td>
</tr>
<tr>
<td>5.2</td>
<td>Future challenges</td>
<td>166</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Mapping chemical composition in 3D</td>
<td>166</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Future experiments</td>
<td>167</td>
</tr>
<tr>
<td>5.2.3</td>
<td>Upscaling problem</td>
<td>168</td>
</tr>
<tr>
<td>5.3</td>
<td>Concluding remarks</td>
<td>170</td>
</tr>
</tbody>
</table>

## References

171

## Appendices

<table>
<thead>
<tr>
<th>Appendix</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Supplementary material</td>
<td>195</td>
</tr>
<tr>
<td>A.1</td>
<td>Computing Resources</td>
<td>195</td>
</tr>
<tr>
<td>B</td>
<td>Supplementary material to Kråkeneset gabbros</td>
<td>197</td>
</tr>
<tr>
<td>B.1</td>
<td>Introduction</td>
<td>197</td>
</tr>
<tr>
<td>B.2</td>
<td>EBSD results</td>
<td>198</td>
</tr>
<tr>
<td>B.3</td>
<td>4D evolution of grain shapes</td>
<td>203</td>
</tr>
<tr>
<td>B.4</td>
<td>Attempted segmentation methods</td>
<td>207</td>
</tr>
<tr>
<td>B.4.1</td>
<td>Indicator Kriging (IK)</td>
<td>207</td>
</tr>
<tr>
<td>B.4.2</td>
<td>Blob3D</td>
<td>207</td>
</tr>
<tr>
<td>C</td>
<td>Supplementary material to pressure-solution data</td>
<td>209</td>
</tr>
<tr>
<td>C.1</td>
<td>Introduction</td>
<td>209</td>
</tr>
<tr>
<td>C.2</td>
<td>Pore evolution during ongoing pressure-solution processes in NaCl</td>
<td>210</td>
</tr>
</tbody>
</table>
List of Figures

2.1 Tomographic scanner build by Cormack in 1963. Image from Cierniak (2011) ........................................... 16
2.2 Hounsfield laboratory scanner (a) and image of a preserved brain (b). From Cierniak (2011) ....................... 16
2.3 X-rays beam configurations ........................................ 19
2.4 Synchrotron geometry ........................................ 20
2.5 Filtered back-projection explained ................................ 21
2.6 MuCalc spreadsheet calculator ................................ 24
2.7 Image artefacts ........................................ 25
2.8 Example of 3D-DIC application ................................ 28
2.9 3D-DIC explained ........................................ 29
2.10 Position of tomographic data in the thin sections and hand specimen, Kråkeneset gabbros. .................. 31
2.11 Correlation of linear absorption coefficient of the µCT data with mineral compositions. ...................... 32
2.12 Quant3D analysis ........................................ 34
2.13 Statistical Region Merging outputs. ........................ 36
2.14 Summary of segmentation workflow for Kråkeneset gabbros ..................................................... 37
2.15 Global thresholding .......................................... 38
2.16 Vertical slices of the µCT data corresponding to the SEM images ........................................... 40
2.17 Analysis workflow for Kråkeneset gabbros ........................................ 40
2.18 Cell assemblage for pressure-solution experiments ........................................ 42
2.19 Experimental setup of the pressure-solution experiments ........................................ 43
2.20 Test materials for pressure-solution experiments ..................................................... 45
2.21 Graphic interface of Tomowarp2 ................................ 48
2.22 Image analysis denoising filters ................................ 49
2.23 Interactive thresholding ...................................... 50
2.24 Results of “Separated Objects” operator in AvizoFire ..................................................... 51
2.25 Sketch illustrating the effect of separation ........................................ 51
2.26 Effects of different separation algorithms ........................................ 52
2.27 Analysis workflow for pressure-solution data ........................................ 56

3.1 Mineral phases and microstructures present in the metagabbros ..................................................... 62
3.2 BSE images of Kråkeneset samples and corresponding microtomographic datasets ........................................ 66
3.3 Grs-Alm-Py plot showing garnet compositions from EMPA analyses ........................................ 67
3.4 Compositional maps for CaO and MgO for the low (A-C) and high (B-D) strain domains ........................................ 68
3.5 3D renderings of original cropped subvolumes (top) and segmented garnets (bottom) ........................................ 69
List of Figures

3.6 Pore size distribution for garnets grains in eroded and non eroded data. 72
3.7 3D rendering of label analysis of garnets. 73
3.8 Effects of erosion-dilation on morphology (A) and on the degree of interconnectivity (B). 73
3.9 Results of EBSD analysis. 75
3.10 Schematic sketch illustrating the evolution of reaction microfabrics. 77
3.11 Sketch summarising the evolution from an undeformed olivine gabbro towards a deformed omphacite-garnet eclogite. 81

4.1 IPS model by Lehner and Leroy (2004). 89
4.2 Fluid-interface models in PSC. 91
4.3 Examples of stylolites in different rock types. 95
4.4 Strain shadows and strain caps. 97
4.5 Compaction curves for pure NaCl samples. 101
4.6 Vertical µCT slices of control experiment. 102
4.7 Analysis of preliminary experiment. 102
4.8 Vertical µCT slices of pure NaCl samples. 104
4.9 Compaction curves for the NaCl-biotite/kaolinite samples. 106
4.10 Vertical µCT slices of NaCl-biotite samples. 107
4.11 Compaction curves for NaCl-glass beads. 109
4.12 Vertical µCT slices of NaCl-glass beads and NaCl-glass beads-biotite samples. 110
4.13 Evolution of biotite thickness, porosity and strain partitioning in NaCl-biotite sample, second run. 113
4.14 Porosity as a function of the vertical loading axis z. 114
4.15 3D renderings of a subvolume from the NaCl-biotite sample, showing the evolution of pores and biotite with increasing compaction. 114
4.16 Bulk porosity evolution. 116
4.17 Pore size distributions for different samples as a function of vertical shortening. 118
4.18 Pore size distribution in the marginal NaCl layers (A) and in central biotite layer (B) for NaCl-biotite sample in the second run (6.64 MPa). 120
4.19 Cumulative plots for pure NaCl samples and NaCl-biotite. 121
4.20 Cumulative plots for NaCl-glass beads, and NaCl-biotite-glass beads samples. 123
4.21 Shape factor plots for pure NaCl and NaCl-biotite samples. 124
4.22 Evolution of the pore space interconnectivity in different experiments with increasing compaction. 127
4.23 3D renderings of NaCl-biotite skeleton. 128
4.24 Skeleton analysis for NaCl-biotite sample. 129
4.25 3D rendering of NaCl-GB-biotite skeleton. 130
4.26 Outputs of volumetric 3D-DIC for maximum shear strain. 132
4.27 Outputs of 3D-DIC for volumetric strain. 133
4.28 Strain rates for the maximum shear strains calculated from 3D-DIC outputs. 136
4.29 Strain rates for the volumetric strains calculated from 3D-DIC outputs. 137
4.30 SEM SE images of recovered samples. 140
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.31</td>
<td>Best-fits of compaction curves</td>
<td>143</td>
</tr>
<tr>
<td>4.32</td>
<td>Vertical µCT slices showing the evolution of the NaCl-GB-biotite sample over time</td>
<td>144</td>
</tr>
<tr>
<td>4.33</td>
<td>Model for stylolite growth and propagation in the performed experiments</td>
<td>147</td>
</tr>
<tr>
<td>4.34</td>
<td>3D renderings of a subvolume from the sample NaCl-biotite-glass beads showing the evolution of pores, biotite and glass beads with increasing compaction</td>
<td>150</td>
</tr>
<tr>
<td>4.35</td>
<td>Schematic models for PSC in sample NaCl-glass beads.</td>
<td>151</td>
</tr>
<tr>
<td>4.36</td>
<td>Possible precipitation sites</td>
<td>152</td>
</tr>
<tr>
<td>4.37</td>
<td>Pore size distribution with lower threshold at 125 cubic voxels.</td>
<td>155</td>
</tr>
<tr>
<td>B.1</td>
<td>EBSD results of low strain domain (sample 066B2)</td>
<td>198</td>
</tr>
<tr>
<td>B.2</td>
<td>EBSD results of low strain domain (sample 066B2)</td>
<td>199</td>
</tr>
<tr>
<td>B.3</td>
<td>EBSD results of intermediate strain domain (sample 0617)</td>
<td>200</td>
</tr>
<tr>
<td>B.4</td>
<td>EBSD results of high strain domain (sample 0618)</td>
<td>201</td>
</tr>
<tr>
<td>B.5</td>
<td>EBSD results of high strain domain (sample 0618)</td>
<td>202</td>
</tr>
<tr>
<td>B.6</td>
<td>Outputs of segmentation for olivine (green) and garnet (blue) grains, in the low strain domain (different viewing angles)</td>
<td>203</td>
</tr>
<tr>
<td>B.7</td>
<td>Label analysis of intermediate strain domain after erosion</td>
<td>203</td>
</tr>
<tr>
<td>B.8</td>
<td>Quant3D results on eroded data for the Kråkeneset gabbros.</td>
<td>204</td>
</tr>
<tr>
<td>B.9</td>
<td>Tabulation of representative garnet structural formulae for the low (066B2) and high (0618) strain domain obtained from the microprobe analyses.</td>
<td>204</td>
</tr>
<tr>
<td>B.10</td>
<td>Indicator Kriging</td>
<td>207</td>
</tr>
<tr>
<td>B.11</td>
<td>Outputs of Blob3D segmentation</td>
<td>208</td>
</tr>
<tr>
<td>C.1</td>
<td>Flynn diagrams for NaCl-biotite and NaCl-glass beads samples.</td>
<td>211</td>
</tr>
<tr>
<td>C.2</td>
<td>Flynn diagrams for pure NaCl and NaCl-biotite samples, compacted for 2465 hours</td>
<td>212</td>
</tr>
<tr>
<td>C.3</td>
<td>Flynn diagrams for pure NaCl and NaCl samples, compacted for 2465 hours, after Border Kill operator in Avizo</td>
<td>213</td>
</tr>
<tr>
<td>C.4</td>
<td>Orientation of pores for first run of experiments</td>
<td>213</td>
</tr>
<tr>
<td>C.5</td>
<td>Pores orientations for samples compacted for 2465 hours.</td>
<td>214</td>
</tr>
<tr>
<td>C.6</td>
<td>Pores orientations in biotite and NaCl layers within the NaCl-biotite samples, compacted for 2465 hours</td>
<td>215</td>
</tr>
</tbody>
</table>
List of Tables

1.1 Tabulation of applications in which time-resolved µCT has been used to investigate aspects of fluid-rock interaction processes. 7

2.1 Tabulation of the informations acquired for each 2D analytical technique. 30

4.1 Tabulation of the experimental conditions for each the experiments performed. 99

4.2 Tabulation of pore size evolution for increasing strain and different sample compositions. Grey box highlights the values for the pure NaCl experiments. 122

4.3 Tabulation of pore connectivity for increasing strain and different sample composition in the analysed subvolume (400³ voxels). Tot. pore space refers to the total pore space included in the analysed subvolume. Grey box highlights the values for the pure NaCl experiments. 126

4.4 Tabulation of skeletonization analyses for increasing strain and different sample composition in the analysed subvolume (400³ voxels). Tot. pore space refers to the total pore space included in the analysed subvolume. 130

4.5 Tabulation of 3D-DIC results for increasing strain and different sample composition. Strain rates in [s⁻¹]. 138

A.1 The table lists the computing resources used for each data, and the specifics. 196

B.1 Electron microprobe chemical compositions of oxides in garnets, used to calculate the x-ray absorption coefficients. 199

B.2 Frequency distribution data for non-eroded data. The first column of each dataset refers to absolute frequency, the second one to the cumulative frequency relative to the total amount of garnet in each sample. 205

B.3 Frequency distribution data for eroded data. The first column of each dataset refers to absolute frequency, the second one to the cumulative frequency relative to the total amount of garnet in each sample. 206
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>2-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>3-dimensional</td>
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<tr>
<td>4D</td>
<td>4-dimensional</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
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<tr>
<td>EMPA</td>
<td>Electron MicroProbe Analyser</td>
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<tr>
<td>EBSD</td>
<td>Electron Back-Scattered Diffraction</td>
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<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
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<td>XRD</td>
<td>X-ray powder diffraction</td>
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<td>µCT</td>
<td>Computer x-ray micro-Tomography</td>
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<td>sµCT</td>
<td>synchroton Computed x-ray micro-Tomography</td>
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<tr>
<td>3D-DIC</td>
<td>Volumetric Digital Image Correlation</td>
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<td>Ab</td>
<td>Albite</td>
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<td>Alm</td>
<td>Almandine</td>
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<td>Cpx</td>
<td>Clinopyroxene</td>
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<td>Czo</td>
<td>Clinozoisite</td>
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<tr>
<td>Ep</td>
<td>Epidote</td>
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<td>Grt</td>
<td>Garnet</td>
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<td>Grs</td>
<td>Grossular</td>
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<tr>
<td>Ilm</td>
<td>Ilmenite</td>
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<tr>
<td>Ol</td>
<td>Olivine</td>
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<tr>
<td>Opx</td>
<td>Orthopyroxene</td>
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<tr>
<td>Pl</td>
<td>Plagioclase</td>
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<tr>
<td>Py</td>
<td>Pyrope</td>
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<tr>
<td>Sympl</td>
<td>Symplectites</td>
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<tr>
<td>GB</td>
<td>Glass beads</td>
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"We must become the change we want to see in the world".

—Mahatma Gandhi
1.1 Natural and experimental fluid-rock interaction

Fluid-rock interaction constitutes one of the main processes that contribute to the deformation of rocks, present at both the crust and mantle conditions. This interaction causes substantial petrophysical and geochemical modifications in terms of compositions and textures, with important implications for rock geochemistry and geodynamics (Jolivet et al., 2005; Yardley, 2009; Jamtveit and Austrheim, 2010; Harlov and Austrheim, 2013; Jonas et al., 2014). During replacement reactions, the interaction with fluids can lead to the formation of transient porosity, thereby influencing porosity and permeability properties of the rock. Evolving porosity is important for oil and gas reservoirs, as it modifies fluid pathways (Urai et al., 1986; Spiers et al., 1990; Bjørkum et al., 1998; Ehrenberg, 2006; Ghanbarzadeh et al., 2015). It is also important for the hydro-mechanical stability of slopes (Croizé et al., 2010) and elastic wave propagation velocity (Christensen and Szymanski, 1991; Vanorio et al., 2008; Croizé et al., 2010; Jamtveit and Austrheim, 2010). Successful management of hydrocarbon reservoirs and radioactive waste disposal critically depends on the detailed knowledge of dynamic transport properties, such as porosity and permeability (Spiers et al., 1990; Chaturvedi, 1993).

1.1.1 Fluid-rock interaction in nature

When fluid-rock interaction is associated with metamorphic conditions and processes, the process is called metasomatism. According to Harlov and Austrheim (2013), the scientific definition of metasomatism is "a metamorphic process by which the chemical composition of a rock or rock portion is altered in a pervasive manner and which involves the introduction and/or removal of chemical components as a result of the interaction of the rock with aqueous fluids (solutions)." During metasomatic processes, mineral reactions occur, which affect the thermodynamic properties of rocks and induce regional-scale transformations (Austrheim, 1987; Austrheim et al., 1997; John and Schenk, 2003; John et al., 2009; Labrousse et al., 2010; Putnis and Austrheim, 2010; Angiboust et al., 2014). Fluid-mediated metamorphic reactions can reduce the mechanical strength of rocks, with important implications for large-scale geodynamics and for lithospheric density (Jackson et al., 2004; Kaus et al., 2005).

When associated with subduction processes, fluid infiltration is coupled with arc volcanism, ore deposit formation and substantial element transport (Kerrick and
Chapter 1. Introduction

Connolly, 2001; Lund and Austrheim, 2003; Jamtveit and Austrheim, 2010). If fluids are released during dehydration reactions in eclogitization processes, they can reactivate previously hydrated faults. The presence of fluids can lower effective stresses and induce seismic failure (Kirby et al., 1996) or cause disequilibrium metamorphism reactions, which can affect strain localisation in the crust (Jamtveit et al., 2016). In the presence of preferential fluid pathways (i.e. cracks), fluid-rock interaction leads to the localisation of deformation processes and mineral reactions, introducing important anisotropies for permeability properties and/or rock weathering (Røyne et al., 2008).

At low-grade metamorphic and diagenetic conditions, the interplay between fluid-rock interaction and rock deformation can cause the localisation of pressure-solution. This is a solution mass transfer mechanism in which material is dissolved and re-precipitated following a stress and chemical potential gradient (Rutter, 1983; Gratier et al., 2013). The localisation of the pressure-solution in rocks causes the formation of stylolites. Stylolites represent rough surfaces of pressure dissolution seams, some of which contain precipitated insoluble material (Park and Schot, 1968; Rutter, 1983). Where they redirect fluid flow in the rock, it is crucial to understand their nature, origin and growth dynamics (Heap et al., 2014; Gratier et al., 2015). Despite numerous experimental studies and numerical models, the current knowledge of pressure-solution lacks a complete spatio-temporal characterisation of the evolving porosity (Gratier, 1987; Cox and Paterson, 1991; Renard, 2004; Gratier et al., 2005; Koehn et al., 2012). Only recently, few studies have attempted to contribute to a better comprehension of the dynamic evolution of porosity during ongoing pressure-solution (cfr. chapter 4, see section 4.2.2), but there is no clear understanding of the mechanisms active at the microscale and on the evolution of porosity around propagating stylolite tips (Carrio-Schaffhauser et al., 1990; Aharonov and Katsman, 2009). Furthermore, the role of stylolites in controlling fluid flow remains unsettled (cfr. Heap et al., 2014).

Natural microfabrics that formed during fluid-rock interaction constitute frozen snapshots from the tectono-metamorphic history of the rock. However, they do not generally allow to unravel the progressive evolution of the microfabrics, unless earlier time-frames are preserved in local domains. In cases where the original rock is not preserved, reconstruction of the fluid-rock interaction history is important to address, as well as the understanding of how the interplay affected the original structure and composition of the rock. Many questions regarding the modifications occurring on the pore/grain scale and how they affect the macro-properties of the rock still remain to be addressed. In the last few decades, many experimental studies and numerical
models have investigated physical and geochemical aspects of fluid-rock interaction to identify the mechanisms active at the pore/grain scale, and provide a better understanding of the processes at larger scale. These studies mostly investigated fluid-rock interaction and the microstructural and microchemical changes involved in 2D analyses. Despite the effort of these research studies, continued exploration of this area arises new questions on the spatio-temporal evolution of the process at the microscale.

1.1.2 2D laboratory investigations of fluid-rock interaction

Amongst the laboratory investigation of fluid-rock interaction, many studies analysed precipitation/dissolution, replacement reactions and fluid flow properties. Some examples of these studies are described here. Spiers and co-workers studied pressure-solution in NaCl, assessing the microstructural changes at grain contacts, and comparing the results with theoretical solutions (Spiers et al., 1990; Schutjens and Spiers, 1999). They found that the processes are enhanced if brine and phyllosilicates are present in the system (Spiers et al., 1990; Bos et al., 2000a; Bos and Spiers, 2000, 2001). Pressure-solution was also investigated by Renard and co-workers in compaction experiments and numerical modelling (Renard et al., 2000). In these studies, they observed that the process is accelerated in the presence of clays (Renard et al., 2001), confirming the results of Spiers et al. (1990) and Hickman and Evans (1995) (cfr. chapter 4, see section 4.2.2).

Ayers and Watson (1993) conducted experimental studies to quantify apatite/fluid partitioning during fluid-rock interaction mechanisms, as apatite controls rare earth elements (REE) partitioning during fluid-rock interaction. It is important to predict trace elements contents of coexisting fluid and rocks. Steefel and Lasaga (1994) numerically modelled precipitation/dissolution reactions in fractured hydrothermal systems, to assess the relation between reaction-induced porosity and permeability changes. The study revealed that permeability may be enhanced where fluids move up temperature, and may cause channelling of flow.

In other studies, the interaction of CO$_2$-rich fluids on the geochemical and petrophysical properties of rocks was investigated to understand the effects of potential CO$_2$ geological storage sites. Dobson et al. (2003) conducted experimental studies and numerical modelling to investigate the porosity and permeability changes associated with dissolution-precipitation mechanisms caused by heat-generating radioactive waste in a deep underground disposal facility. CO$_2$ was dissolved in distilled water and injected in tuff core plugs. Experimental conditions very closely resembled temperature, pressure and chemical compositions values of the repository.
Results showed that over time fracture sealing occurred; however, at the repository conditions this is unlikely to occur as it would require much longer period of heating ($10^3$ to $3 \times 10^6$ ys) than under laboratory conditions. Shogenov et al. (2015) studied and quantified the interaction of CO$_2$-rich fluids on the properties of rocks in numerical and experimental models for a site in the Baltic Region, as part of a Carbon Capture Storage (CCS) project. The study revealed a substantial increase in porosity and permeability, which induced a decrease in bulk and matrix density and P and S wave velocities.

More recently, Jonas et al. (2014) performed experimental studies of fluid-rock interaction to investigate reaction front propagation, through replacement of calcium carbonate by apatite-forming reactions. The replacement reaction created grain boundaries and transient porosity that acted as fluid pathways. The results indicated that grain boundaries are a much more effective fluid pathway compared to the transient porosity newly formed. Replacement reactions during fluid-rock interaction were also explored by Putnis and Putnis (2007), Jamtveit et al. (2009), Putnis and John (2010), and Ruiz-Agudo et al. (2014), whose studies reported creation of transient porosity to accommodate the overall change in volume.

Although these studies achieved important conclusions on the relationship between porosity and permeability and were able to relate the micro-scale properties to the macro-scale, they do not characterise the 3D dynamic evolution of fluid-rock interaction. In particular, they were not able to characterize i) the 3D distribution of transient porosity and mineral phases, ii) determine the connectivity of the pore space over time and how this affects fluid percolation, or iii) quantify transport distances and reaction propagation fronts in 3D, all important parameters to reconstruct the deformation history of the rock. These constitute important factors to determine, as metamorphic microfabrics are usually investigated to derive information on P-T-t conditions as well as on deformation mechanisms, active fluid pathways and transport distances (Putnis and Austrheim, 2010). However, they are usually analysed in two dimensions and they report on a static picture from the complex history of fluid-rock interaction. What appears to be entirely enclosed in two dimensions (e. g. coronas) might instead represent an open structure, in which fluids are free to move and elements can be transported elsewhere, hence affecting the reaction propagation fronts (cfr. chapter 3, and Hughes et al., 2016). The degree of interconnectivity and size distributions are similarly important: connectivity of mineral phases and pore space might be hidden in the third dimension. Particular size classes may be the product of deformation mechanisms, and their 3D distribution reflects the direction and extent of the deformation (Menegon et al., 2015). These observations can not be obtained from 2D classical analyses exclusively, as information derived from the third dimension.
1.1 Natural and experimental fluid-rock interaction

(and fourth dimension, e.g. time) may contribute to the interpretations. The dynamic evolution of porosity and permeability properties during fluid-rock interaction and the observed formation of transient porosity during replacement reaction also raise important questions on the evolution of dynamic transport properties during these processes. Addressing these questions naturally requires a characterization of the process in four dimensions, where the fourth dimension is time or strain.

1.1.3 4D characterization of fluid-rock interactions

Geophysical and field-based investigations provide good characterization of the 3D large-scale aspects of the processes, but they are unable to identify the processes occurring at micro-scale and at grain interfaces. An attempt to provide a time-resolved characterization of fluid-rock interaction at the micro-scale was made by Vanorio (2015). Using time-lapse SEM images of CO$_2$ injected in carbonates and sandstones under stress, the author monitored the petrophysical properties of the rocks before and after injection, including porosity, elastic waves, permeability and pH of the fluid. Despite the innovative approach, the technique required preparing SEM samples, and the performed visualisation were done in two dimensions, loosing information on the third dimension.

With the advance of Computed X-ray micro-Tomography (µCT), the spatial distribution of porosity and mineral phases can now be addressed in three dimensions, providing new insights into the micro-scale variability emerging during fluid-rock interaction (cfr. chapter 3, section 3.1 and chapter 4, section 4.2.2). The recent development and growing availability of µCT in the geosciences has allowed experimental scientists to directly investigate a range of different natural processes in three dimensions and observe their evolution in time (4DµCT) without destructive testing of the rock samples. In this technique, samples are positioned on a rotary stage in front of an X-ray source, and 2D radiographs are recorded at increasing angles while the sample rotates around its vertical axis in front of a detector. A reconstruction algorithm converts the 2D radiographs into a 3D tomographic dataset allowing investigation of each phase in the sample in three or four dimensions. A detailed description of the technique is given in chapter 2, section 2.2.

In 4DµCT, the fourth dimension can represent any progress coordinate such as time, strain, reaction progress, temperature or pressure. Advances in experimental equipment allow for laboratory temperature and pressure values close to reservoir conditions. This provides a means to monitor ongoing processes similar to in-situ reservoir conditions (Fusseis et al., 2014a). In recent years, µCT has been used in different applications, including time-resolved investigation of fluid-rock interaction.
Table 1.1: Tabulation of applications in which time-resolved µCT has been used to investigate aspects of fluid-rock interaction processes.

<table>
<thead>
<tr>
<th>Application</th>
<th>Papers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity quantification</td>
<td>Clausnitzer and Hopmans (2000), Bernard (2005),</td>
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<tr>
<td></td>
<td>Cai et al. (2009), Navarre-Sitchler et al. (2009),</td>
</tr>
<tr>
<td></td>
<td>Armstrong and Ajo-Franklin (2011), Silin et al. (2011), Fusseis et al.</td>
</tr>
<tr>
<td></td>
<td>(2012), Berg et al. (2013), and Noiriel (2015)</td>
</tr>
<tr>
<td>Dynamic process</td>
<td>Crestana et al. (1985), Renard et al. (2004), Gaye et al. (2014),</td>
</tr>
<tr>
<td></td>
<td>and Ghanbarzadeh et al. (2015)</td>
</tr>
<tr>
<td>Fluid-flow analyses</td>
<td>Wildenschild et al. (2005), Carminati et al. (2008), and Andrew et</td>
</tr>
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<td>al. (2014, 2015)</td>
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These studies demonstrated the capability of µCT to monitor and characterise the evolution of porosity and dynamic processes. The combination of these observations with the information obtained through 2D analyses further provides a multi-dimensional characterization of the processes at the microscale.
1.2 Research motivations

Despite these pioneering time-resolved fluid-rock interaction studies, the induced petrophysical and geochemical variations occurring at microscale remain poorly understood. Consequently, important open questions await to be addressed:

- How do fluid-rock interaction processes evolve in time and space?
- How are the dynamic transport properties and permeability of a rock affected during fluid-rock interaction?
- How do porosity and mineral phases spatially distribute, and how do they evolve in time?

A complete spatio-temporal characterisation of the evolving microstructures is needed to understand the dynamic evolution of the process at the pore/grain scale. This thesis investigates two fluid-rock interaction mechanisms: 1) eclogitization coupled with fluid infiltration and strain localisation in natural rock samples; and 2) pressure-solution processes using NaCl as rock analogue. These two studies aim to provide a multi-dimensional characterization and new insights into the process by using 4DµCT.

The first case-study investigates natural rock-samples from Western Norway, which show a compositional change from olivine-rich metagabbros to omphacite-garnet bearing eclogites in a ductile shear zone (see chapter 3). The eclogites are localised in narrow shear zones, which allowed an external input of fluid into the rock to localise eclogitization. The samples show a compositional transition from olivine gabbros to omphacite-garnet eclogites along a strain gradient. The studied samples were taken across this strain gradient, which represents the fourth dimension. In this study µCT was applied in combination with classic 2D techniques (SEM, EDS, EMPA, EBSD) to identify the interplay between mineral reactions, fluid infiltration and strain localisation. In particular, the three-dimensional spatial distribution of garnets was investigated as a function of strain. Interconnectivity of garnets provides useful insights into the rheological behaviour of this mineral, which has been controversially discussed over recent years (see chapter 3, section 3.1). Moreover, understanding the spatial distribution of garnets in relation to fluid infiltration and strain localisation has strong implications for element transport and fluid flow, and provides additional information on the deformation mechanisms active at the grain-scale.

The second case-study analyses pressure-solution processes using NaCl as rock-analogue, to monitor the evolution of porosity and pore connectivity in four dimensions, where the fourth dimension is time or strain (see chapter 4).
During pressure-solution processes, the petrophysical properties of the rock are highly altered, leading to porosity and permeability changes, which in turn affect fluid percolation. Sieved NaCl samples were uniaxially compacted, and μCT scans were acquired at regular compaction times, allowing characterisation of the vertical shortening of the sample. The evolution in space and time of grain morphologies, pore space and pore connectivity of the samples were also investigated. Conventional image analysis provides good 4D quantification of the grains and porosity distributions, but is unable to capture the internal deformation of the samples. To address these issues, volumetric Digital Image Correlation (3D-DIC) was applied on the reconstructed μCT datasets, as explained in chapter 2, section 2.3.
The structure of the thesis reflects the research motivations outlined in section 1.2. The two case-studies have been described and analysed separately, therefore description of the relevant literature reviews are included within each data chapter. In particular:

- **Chapter 2** describes the image processing workflow adopted to analyse the two datasets. It is divided in two parts, as the nature and quality of the data required different experimental methods, image acquisition, processing and analysis routines to be developed for the two studies.

- **Chapter 3** This chapter describes the first case-study. Results indicated that the evolution from low to high strain domain reflected an increase in garnet volume, accompanied by the progressive disconnection of garnets into oblate clusters, which defined a mylonitic foliation. EBSD analyses did not reveal any evidence for crystal plasticity, but rather highlighted evidence for minor microfracturing, coalescence and overgrowth. These observations pointed to a mechanical disintegration of garnet coronas with increasing strain, together with the ongoing nucleation and overgrowth of garnets while the rock was deforming.

- **Chapter 4** examines the second case-study, assessing the experimental work on pressure-solution processes. In this chapter, effects of different sample compositions and variable load on pressure-solution were investigated. The results showed that bulk porosity and pore connectivity are reduced with increasing strain if phyllosilicates are present in the system. Particularly, strain was accommodated differently between the phyllosilicates and pure NaCl layers. In the case of incompressible and insoluble glass beads being added to the sample, porosity retained its connectivity with increasing strain, although it became more disconnected if phyllosilicates are present. Furthermore, phyllosilicates progressively wrapped around glass beads, forming strain caps. In the pure NaCl samples, porosity retained its connectivity even at the highest level of strain.

- **Chapter 5** summarises and discusses the main findings in the frame of fluid-rock interaction. It also discusses limitations of µCT techniques, spatial resolution problems and upscaling issues. I then describe ideas for future research.

- **Appendix A** reports a tabulation of computing resources used and the technical specifications. It also describes which computing resources have been used in
Chapter 1. Introduction

each case-study.

- **Appendix B** includes additional information on chapter 3. These include complete EBSD results, chemical composition (Table B.1), tabulations of frequency size distribution from label analyses for eroded and non eroded data (Table B.2, Table B.3), and results from Quant3D analyses. It also includes a brief description of segmentation techniques that did not work.

- **Appendix C** described additional information on chapter 4. These include additional images to show the evolution of pore shape and orientation for different sample compositions with increasing strain.
Methods and materials
2.1 Introduction

Within this chapter, I describe the background theory and principles of synchroton and laboratory microtomography. This is followed by a description of the specific analytical, experimental and data analysis techniques and approaches applied to this project.

To fully characterize the dynamic behaviour of porosity and fluid pathways in four dimensions, I have built an innovative work-flow which combines together classical analytical techniques (optical microscope, SEM, EDS and EBSD) with advanced micro-CT data acquisition and image analysis. While classical analytical techniques provide 2-dimensional analyses, micro-CT data extend these informations to the 3rd and 4th dimension, to create a multi-dimensional characterization of the data. Each of these techniques provide a particular kind of information, which combined together with digital image analysis can help to understand the spatio-temporal evolution of fluid flow and porosity. The first part of this chapter describes the methods used for the 4-dimensional analysis of mineral reaction microfabrics from a ductile shear zone, using the sample distance from the shear zone as a proxy for deformation and time (fourth dimension). Natural samples of a ductile shear zone were investigated with classical microscopy and chemical microanalysis, to characterize the morphological evolution of garnets along a strain gradient. However, these analyses alone are not sufficient to understand the dynamic evolution of garnets in four dimensions (three spatial dimensions and strain being the 4th dimension), which potentially plays a key role in controlling the rheological behaviour of a rock and re-directing fluid flow. Hence, µCT was applied to investigate the spatial evolution of garnet grains in relation to the strain.

In the second part of this chapter, I present the experimental equipment and approach and data analysis methods used in a 4-dimensional study of pressure-solution driven deformation in NaCl. In that study, time and vertical shortening are used to define the fourth dimension. Controlled experiments using NaCl grains as a rock -analogue were performed to monitor the compaction over time and the deformation of the samples using laboratory X-ray microtomography. Conventional image analysis was combined with volumetric Digital Image Correlation (3D-DIC) to quantify the internal deformation of the sample (cfr. section 2.3).
Chapter 2. Methods

2.2 Computed X-ray microtomography

2.2.1 A history of computed X-ray microtomography

The term Tomography derives from the Greek word tomos meaning "slice" and graphia meaning "writing". The technique relies on the interaction between X-rays and matter. X-ray radiation is an electromagnetic radiation, with wavelengths ranging from 0.01 to 10 nanometers and energies in the range 100 eV to 100 keV. X-radiation was discovered in 1895 by Wilhelm Conrad Röntgen, later awarded in 1901 the Nobel Prize in physics (Cierniak, 2011). Röntgen was analysing the glow that occurred during electric discharges inside an evacuated glass tube, known as Crookes tube, and in particular the properties of cathode rays, when he suddenly noticed that a screen made of fluorescent paper started to glow. During his discovery, Röntgen carried out a series of experiments, in which he places different objects between the tube and the screen. It was then that he also noticed the skeleton of his own hand outlined on the screen. This discovery led to a great success, especially in the field of medicine, leading to the development of X-ray photographs with the purpose of investigating the internal characteristic of a person without surgery. In 1897, the first picture of a whole skeleton was taken using X-rays by William Morton. The first attempt to obtain a three-dimensional X-ray scan was carried by E. Thompson using the principles of stereography: two pictures of an immobile patient were taken at different angles, and viewed using a stereoscope. However, the technique was computationally demanding (Cierniak, 2011). It was only with further refinement of computational techniques that the current approach to X-ray computed tomography was born, thanks to Godfrey Hounsfield and Allan Cormack, later awarded in 1979 with the Nobel Prize in Physiology or Medicine (Hounsfield, 1976; Cierniak, 2011). In 1963, while employed at Tufts University, Cormack carried a test experiment in his own built apparatus to confirmed the theoretical solution to the problem of image reconstruction (Figure 2.1) (Cormack, 1973). The practical application was, however, exploited by the engineer Godfrey Hounsfield: while employed at the Central Research Laboratories in EMI Ltd., he successfully developed the first CT scanner (Cierniak, 2011). In 1967, he developed a new method to improve image reconstruction, thanks also to the computational resources available for the complicated calculations needed. The first experiments, using gamma radiation, were carried out successively. Despite low resolution and numerous scanning hours, a first image was obtained with enough contrast to differentiate brain tissues. The machine (Figure 2.2) was patented in the following year. In subsequent tests, using X-ray radiation, Hounsfield was able to
2.2 Computed X-ray microtomography

shorten the scanning time to 9 hours, and the reconstruction time to 20 minutes. The first patient scan was carried out in 1971, to investigate a brain tumour. In 1973, the acquisition time for an image was reduced to 20 s, and the resolution of the image increased from 80 x 80 pixels to 320 x 320 pixels (Cierniak, 2011).

Figure 2.1: Tomographic scanner build by Cormack in 1963. Image from Cierniak (2011).

Figure 2.2: Hounsfield laboratory scanner (a) and image of a preserved brain (b). From Cierniak (2011).

2.2.2 Principles of a µCT system

Computed X-ray Microtomography is based on the interaction of X-rays with the investigated materials. The intensity of incident X-rays as they pass through an object is decreased as a function of composition and density of the object, which define the extent of the interaction of X-ray photons with the object (Landis and Keane, 2010; Baker et al., 2012). At lower energies (< 100 keV), the process of
X-ray attenuation occurs by means of a photoelectric effect, in which the photons energy is totally transferred to an electron as they interact with an atom. The extent of attenuation through the photoelectric effect is related to the power of the mean atomic number of the sample (Ketcham, 2005b; Wildenschild and Sheppard, 2013; Willmott, 2013). Lower atomic number (Z) elements generally absorb less than high Z elements (Landis and Keane, 2010). At higher energies (keV > 100), the X-ray attenuation process is dominated by Compton scattering and the extent of interaction is approximately proportional to the material density (Ketcham, 2005a; Landis and Keane, 2010; Wildenschild and Sheppard, 2013; Willmott, 2013). During Compton scattering, the photons transfer part of their energy to an electron in the atom, which is ejected and deflected in a different direction (Ketcham and Carlson, 2001). The decrease of intensity for a monochromatic beam of X-rays through a homogeneous material can be described by the Lambert-Beer law:

\[ I = I_0 \exp \left[ -\int_{-\infty}^{\infty} \mu(x) \, dx \right] \]

where \( I_0 \) represents the incident intensity of the X-rays, \( I \) is the attenuated intensity after X-rays have passed through a sample of thickness \( x \), and \( \mu(x) \) is the linear attenuation coefficient (Ketcham and Carlson, 2001; Cnudde and Boone, 2013). This equation states that the intensity of a monochromatic beam decreases exponentially as a function of the line integral of the linear attenuation coefficient along the X-ray path (Ketcham and Carlson, 2001; Baker et al., 2012; Fusseis et al., 2014b; Kyle and Ketcham, 2015). However, samples are most likely to be multi-phasic and inhomogeneous materials and the beam, unless a monochromator is used, is generally polychromatic (variable energy, Wildenschild and Sheppard, 2013). In these cases, the extent of attenuation is a complex integral of the path length and attenuation coefficients for all materials in the object \( (\mu_i) \) and all energies in the incident X-rays (Ketcham and Carlson, 2001; Wildenschild and Sheppard, 2013; Kyle and Ketcham, 2015). For multi-phase materials, the equation thus becomes:

\[ I = I_0 \exp \left[ -\sum_i \mu_i x_i \right] \]

The equation needs to be solved over the full range of of X-ray spectrum for a polychromatic beam (Ketcham and Carlson, 2001; Kyle and Ketcham, 2015).
2.2 Computed X-ray microtomography

2.2.2.1 µCT system

In contrast to a medical CT scanner where the source-detector system rotates around the patient, in material science, during data acquisition, the source-detector system remains fixed and the sample is positioned on a rotary stage between the X-ray source and an X-ray detector. The detector collects the X-rays passing through the sample by means of a scintillator screen that converts the X-rays into photons of visible light in response to the absorption of X-ray photons (Baker et al., 2012; Wildenschild and Sheppard, 2013; Fusseis et al., 2014b). The photons of visible light are then counted, recorded and converted into a digital signal by amorphous silicon sensors (traditionally charge-coupled devices, named CCD, or by complementary-metal-oxide-semiconductor (CMOS) sensors in modern laboratory scanners (Wildenschild and Sheppard, 2013). Recently, CCD devices have been replaced with thin film transistor arrays (FFT) (or flat panel detectors) as they are considered more modern and advanced in technology (Seibert, 2006). An extensive review of scintillator types is described in Willmott (2013). 2D radiographs of the samples are then recorded in evenly spaced angular intervals through a full rotation of either 180° or 360°, depending on the beam geometry (Figure 2.3): 180° is the final rotation angle for a parallel beam (e. g. synchroton facilities) and 360° is the final rotation angle for a fan or cone-beam geometry (laboratory CT scanners). A successful reconstruction of the sample geometry requires collecting sufficient number of radiographs during a full rotation. The combination of reconstructed 2D slices allows to create a complete 3D reconstructed dataset, composed of 3D pixels, called voxels, and mapped in grey values (see section 2.2.3). Dense mineral phases have a high attenuation coefficients compared to less dense minerals, and appear as bright objects in the reconstructed tomographic data.

2.2.2.2 Synchroton vs laboratory CT scanner apparatus

In the case studies analysed in this thesis, data from both synchroton and laboratory X-ray scanner apparatus are used. The principles of the data acquisition techniques are the same in synchroton and laboratory CT scanner apparatus, however they differ considerably in the way the X-rays are produced and in scanner geometry. In laboratory scanners, the X-rays are produced in X-ray tubes where an electron beam is accelerated onto a target. When the target is hit, the electromagnetic interaction of the electrons with the atoms originates a continuous radiation, that reflects the decelerated emission of electrons: this background signal is called Bremsstrahlung (Willmott, 2013). Characteristic X-ray energies for the type of atom from which they originate are then superimposed on the bremsstrahlung signal on the form of sharp peaks (Ketcham and
Chapter 2. Methods

Figure 2.3: The figure illustrated the two most common geometries for X-ray beams: a) nearly-parallel X-ray beam, synchrotron facilities. Final rotational angle is 180°. b) Cone or fan beam geometry, laboratory CT scanner. Final angle equal to 360°rotation.

Carlson, 2001; Willmott, 2013; Fusseis et al., 2014b).

In synchrotron facilities, the X-rays are produced using circular storage rings, in which electrons are accelerated to near-relativistic speeds (Figure 2.4 A). The electrons are forced to travel in the circular paths by bending magnets and in doing so the electrons emit X-rays. When moving electrons change directions, a narrower X-rays beam is originated in the same direction as the electron motion (Willmott, 2013). The bending magnets allow the electromagnetic beam to be directed in a very focussed cone tangentially to the storage ring: the long distance between the magnet and the sample results in a partially coherent X-ray beam (Figure 2.4 B). Other magnets (wigglers and undulators) can be used to further focus the electron flux and produce an even brighter electromagnetic signal (Willmott, 2013). Monochromator and additional filters can also be used for beam conditioning (Figure 2.4 B). Synchrotron facilities produce very high photon fluxes, enabling rapid imaging and reduced image noise, and monochromatic beams, which allows to "tune" the X-ray to a particular
2.2 Computed X-ray microtomography

energy that prevents beam hardening (see section 2.2.4.2), improving the signal-to-noise ratio (Cloetens et al., 2002; Baker et al., 2012; Fusseis et al., 2014b).

**Figure 2.4:** A) Plan view of a synchrotron facility. B) Schematic plan view of a beamline.

2.2.3 Image correction and reconstruction

The images collected from the X-ray tomograph include the projections (sample scanned at increasing rotational angles), the offset (or dark current) and gain (or flat-field) images which are needed to correct the projections before reconstruction. Offset images record the signal measured in the absence of any X-rays; gain images include images collected with the X-rays on, but without a sample between the beam and the detector. The gain images are important as any heterogeneity they show represents either defects of the incident X-ray beam, energy filters, or a non-uniform response of the detector or scintillator, which can then be removed from the projections. Offset images are needed to correct for detector defects or bias present while the X-rays are off. After gain and offset corrections, the projections are corrected for brightness variations of the X-ray source. This process is called normalisation (Gürsoy et al., 2014).

Once the normalised images are created, the software generates the sinograms which are needed for the reconstruction. The sinogram is a 2D representation in Fourier space of the absorption intensity signal by the pixel row recorded throughout a full 360°rotation in the projections images (Landis and Keane, 2010; Fusseis et al., 2014b). The resulting curve resembles a sinusoid.

The 2D X-ray radiographs are then mathematically reconstructed and converted to tomographic 2D slices by filtered back-projection, based on the "Fourier Slice Theorem" (Landis and Keane, 2010). The data are first processed with a ramp filter through a Fourier transform, and then back-projected. The Ramp filter is applied, in the frequency domain, on the individual rows that share their z-coordinate but
Chapter 2. Methods

at different rotation angles (Kak and Stanley, 1999) and it is needed to improve the quality of the data and avoid "star-like" artefacts. *Back-projection* involves calculating the inverse Fourier transform of the filtered rows, and running each projection back through the image for each rotation angle, using a superimposed square grid (Kak and Stanley, 1999) (Figure 2.5). In this way, a 2D reconstructed tomographic slice is created. The reconstructed 3D dataset consists of horizontal reconstructed tomographic slices stacked together along the z axis in grey scale value. Data acquired using the laboratory CT instrument (see chapter 4) were reconstructed through Octopus software (Dierick et al., 2004), which uses a filtered back-projection reconstruction algorithm. Data acquired at the Advanced Photon Source in Chicago (chapter 3) were reconstructed through the *Tomopy* method, using the gridrec algorithm, similar to the filtered back-projection algorithm (Dowd et al., 1999; Gursoy et al., 2014). In this algorithm, the slice in the Fourier domain is re-sampled on to a Cartesian grid, before being back-projected to the spatial domain. This cartesian grid helps for quick reconstructions. In some cases there is the possibility to scan standards of known composition with the samples (as in being done in many microanalytical techniques) (Jussiani et al., 2016). This allows for a better reconstruction of the sample.

![Filtered back-projection explained](image)

**Figure 2.5:** Filtered back-projection explained. Each sinogram is projected back accordingly to the angle of rotation it was originally recorded. The final backprojected image is obtained by summing all the backprojected views.
2.2 Computed X-ray microtomography

2.2.4 Limitations of µCT systems

2.2.4.1 Pre-reconstruction

The intensities of grey-scale of the phases present in the microtomographic data can be plotted in histograms, where the $x$ axis represents the grey values, and the $y$ axis the absolute frequency of voxels associated with the particular grey value. The presence or lack of a mineral phase is represented in the histogram by a peak or a minimum, respectively. Contrast between the different material has to be sufficient to allow segmentation and reconstruction of the 3D tomographic dataset. When the contrast between different phases is not sufficient, there will be an overlap in the histogram, impeding a good segmentation and optimal reconstruction of the 3D tomographic dataset. This is also the reason why histogram-based reconstruction has not been used in these studies. As mentioned in section 2.2.2, the interaction of photons with the sample depends on the chosen energy (Figure 2.6). The contrast between different phases can therefore be enhanced by varying the energy level and energy used, and it will depend on the density and compositional differences between the phases. The linear attenuation coefficient, which takes into account coherent, Compton scattering and photo-electric effect, will vary accordingly too. The linear attenuation coefficient of various materials can be calculated through the NIST website (National Institute of Standards and Technology) and the XCOM Photon cross-section database (Berger et al., 1998). The University of Texas CT group (R. Hanna and R. Ketcham) created a spreadsheet calculator (MuCalc) which allows the user to plot the linear attenuation coefficients for various materials versus X-ray energy (Figure 2.6). The preliminary comparison of attenuation curves for different materials across the range of X-ray energies enables to understand if there is likely to be sufficient contrast for a good quality scan and the approach can be used to choose the best X-ray energy for the sample to be investigated. I have followed a similar approach in chapter 2, section 2.4.1.2, to correlate the intensities of the reconstructed microtomographic data to the electron microprobe chemical compositions. This approach can be followed only in the case of monochromatic beams, as monochromatic beams eliminate beam hardening artefacts; thus intensity values of reconstructed data should be directly proportional to the measured attenuation coefficient (Tsuchiyama et al., 2005). Similar approaches have been adopted by Tsuchiyama et al. (2005) and Uesugi et al. (2010, 2013), to quantitatively correlate the intensity of the reconstructed images to the linear attenuation coefficient. Tsuchiyama et al. (2005) determined an empirical correlation, which is independent of the material being imaged. A different approach was successively adopted by Tsuchiyama et al. (2013) using dual-CT energy.
Another limitation on image analysis and interpretation is the spatial resolution of the reconstructed image, which should not be confused with the voxel size. The voxel size is defined by the geometry of the instrument or beamline being used to scan the sample. In a synchrotron, it is a function of the pixel size of the camera used to capture projections, and any optical lens used to magnify the image from the scintillator. In a cone-beam laboratory instrument it is defined both by the pixel size of the camera and the geometric magnification given by the ratio of distances between the source, sample and camera. The spatial resolution is more complex and may depend on the sample type (e.g. grain size, composition), sample size, X-ray spot size and the precision of the alignment of the source, rotation axis and camera as well as the geometric factors outlined above. Generally, in a laboratory scanner with cone-beam geometry, the magnification that can be gained is geometrical thus it depends on the ratio of the source object to source camera distance. As this distance gets smaller however, the magnification increases, introducing blurring on the detector plane ($r_3$) (Feser et al., 2008). This blurring effect depends on the X-ray source spot size, the source-object distance ($a$) and the object-detector distance ($b$) (Feser et al., 2008). According to Feser et al. (2008), the real spatial resolution, $r_{total}$, can be calculated through

$$r_{total} = \sqrt{\frac{r_D^2 + r_S^2}{M}}$$

where $r_D$ is detector resolution, and $r_S$ is the resolution of the source spot size, and $M$ is the geometric magnification that takes into account $a$ and $b$. In synchrotron apparatus, the magnification can also be achieved with the use of magnifying optical lenses between the scintillator and the camera (Figure 2.4 B), and the spatial resolution can, therefore, not be calculated using the formula above. In this case, the resolution is estimated from the size of two pixels in the radiograph, according to the Nyquist theorem (Nyquist, 1928; Fusseis et al., 2014b). To avoid confusion within the data chapters, the term resolution will be used to refer to the reconstructed voxel side length, bearing in mind that this is generally smaller than the real spatial resolution.

2.2.4.2 Post-reconstruction

Sometimes, a simple normalization alone is not sufficient to achieve the best reconstruction: this is the reason why most reconstruction packages allow the users to pre-process the images and filter them for artefacts (e.g. beam hardening and ring artefacts), although these pre-filtering algorithms can be applied at any point of the image analysis process.
2.2 Computed X-ray microtomography

Figure 2.6: Linear attenuation coefficients of different phases, through MuCalc spreadsheet calculator.

**Beam Hardening** artefacts appear on the tomographic images as brighter edges compared to the centre (Figure 2.7 A) (Ketcham and Carlson, 2001). These artefacts are caused by shifting of the mean distribution of X-ray spectrum: there is an increase in the mean energy distribution of the beam through absorption of the low-energy of X-rays in a polychromatic spectrum. This causes the X-rays, as they pass through an object, to be more attenuating at short distances (edges) than longer distances (centre), as a result of a decreased attenuation coefficient for any material (Ketcham and Carlson, 2001). Correction for beam hardening artefacts is included in the reconstruction software, through a polynomial algorithm; however it is recommended to control the peak energy (Ketcham and Carlson, 2001). In laboratory CT scanner, it is recommended the use of energy filters to remove low energy X-rays.

**Ring Artefacts** appear as dark or bright circles, full or partial, centred on the rotational axis (Figure 2.7 B). They are caused by anomalous X-ray values given by shifts from individual detectors: the position of the ring corresponds to the area of overlap between these rays during reconstruction (Ketcham and Carlson, 2001). As in the case for beam hardening, ring artefacts can be removed before or after the reconstruction process.

2.2.5 Image Analysis

The 3D reconstructed dataset can be visualised and analysed using digital image analysis. Digital image analysis includes the operations necessary to quantitatively
and qualitatively analyse microtomographic data. It can be divided into:

1. **Pre-processing**: includes filtering the images for e.g. noise removal, resizing, scaling, sharpening; these operations, which can also include image mathematics (subtractions, divisions, etc.) and masking, are performed on the greyscale data.

2. **Segmentation** is the process by which a particular material of interest is selected from the microtomographic images and separated by the other materials by assigning binary values: 1 (white) to the material of interest, 0 (black) to the rest. This process is also called *binarisation* and is a process of image classification. Image segmentation is the most important and can be the most difficult procedure of image analysis: for this reason, over recent years, new segmentation algorithms have been introduced and adopted in most common open-source and proprietary software, in order to address the demanding request for improved image segmentation procedures.

3. **Post-processing** include operations necessary to improve segmented data, such as remove small spots or islands, morphological operations (erosion, dilation, opening, closing), cleaning up from unwanted segmented spots/ phases. These operations are performed on binary data; they can still include masking and image combination.
2.2 Computed X-ray microtomography

4. *Image Analysis* includes characterization, quantification and analysis of each segmented material such as size, shape and orientation analyses.

In Appendix A, a tabulation of the computing resources used to analyse the data, including the software for image analysis, are reported. For the analysis of the Kråkeneset metagabbros, a combination of *ImageJ*® (Schindelin et al., 2012) and *AvizoFire*® v.7 (http://www.fei.com/software/avizo3d/) have been used: *ImageJ*® was used to segment the garnets, while *AvizoFire*® was used to quantify the data, assessing the volume, spatial distribution and connectivity of garnets. Experimental data have been visualised and quantified exclusively in *AvizoFire*® v.8 and *Avizo*® v. 9.

Quantification and analysis of mineral phases are generally conducted through the *Labelling* and *Label Analysis* operators. *Labelling* is a process that identifies and evaluates connected aggregates of voxels belonging to a specified class in segmented data. The degree of interconnectivity depends on the chosen neighbourhood: 6 defines face-connected clusters (e.g. they share at least a face), 18 define clusters with a face or a side in common, 26 defines either a face, a side or a vertex in common. The clusters (or labels) are then identified by different colours. The colours can repeat within the same dataset, as there is a limited number of colours in the map. *Label analysis* (or *Cluster Analysis*) characterises the identified labels on the basis on pre-chosen parameters that the user can select: volume, area, orientation, shape and so on.
2.3 Digital Image Correlation: DIC

Digital Image Correlation (DIC) is a correlation analysis technique, devised to measure displacements, maximum shear and volumetric strains of planar and non-planar surfaces undergoing deformation (Lenoir et al., 2007; Hall et al., 2009). Over the last decade, this technique has been extensively used in experimental geomechanics and in solid and fluid mechanics (PIV or Particle Image Velocimetry) to obtain full-field kinematics and strain field analysis. It has recently increased in popularity, thanks also to the development of non-destructive image techniques, such as X-ray microtomography, where 3D volumes obtained by X-ray microtomography are correlated together to identify internal deformation of the samples and quantify the strains (3D-DIC or Digital Volume Correlation) (Lenoir et al., 2007; Hall et al., 2009, 2012). 3D-DIC can also be used to identify internal structures of the sample, where the strains are high or localised, which otherwise cannot be seen in the images to be correlated, or to quantify porosity evolution in the rock. DIC was performed on the increasingly shortened datasets in chapter 4 (cfr. chapter 2, section 2.5.1.7). The steps that DIC performs on the images (or volumes) involve (Figure 2.9):

1. Definition of nodes distributed over the "reference image" (Figure 2.9, step 1);

2. Definition of the correlation window, which defines the region centred in each node. The initial integer positions in the reference image are defined by the positions of four manually selected vertices. Only nodes within this subset will be analysed. The nodes are chosen semi-automatically on the basis on the grey values in the correlation window, and on the appropriate threshold. This defines the correlation window.

3. Calculation of the correlation coefficient for each displacement of the correlation window within an area (search window) around the target node of the second image;

4. Definition of the actual displacements (discrete displacement) (Figure 2.9, step 2).

5. Sub-pixel refinement and calculation of full 3D strain tensor field from which the maximum shear and volumetric strains are calculated (Lenoir et al., 2007; Hall et al., 2009) (Figure 2.9, steps 3-4).

The strain invariants are calculated from the 3D strain tensor fields according to the following equations. Volumetric strains are calculated through:

\[ \varepsilon_v = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 \]
2.3 Digital Image Correlation: DIC

Figure 2.8: Example of 3D-DIC application. Results from Charalampidou et al. (2011) for 3D-DIC analysis on a sample of a Vosges sandstone deformed under triaxial compression at 130 MPa confining pressure. A) vertical slice through the X-ray tomography volume image after triaxial loading. B, C) Vertical slices, at the same position, through the maximum-shear and volumetric strain volume images, respectively, derived from 3D-DIC analysis of the pre and post-deformation 3D tomography images. Modified from Hall, 2012.

while the maximum shear strains:

\[ \varepsilon_s = \sqrt{\left(\frac{\varepsilon_1 - \varepsilon_2}{2}\right)^2 + \left(\frac{\varepsilon_1 - \varepsilon_3}{2}\right)^2 + \left(\frac{\varepsilon_2 - \varepsilon_3}{2}\right)^2} \]

The subset overlap, which is the overlap given by the node spacing and the correlation window size, defines the resolution and the smoothing of the results. If the correlation window is too large or too small, this will lead to poor correlation (percentages values < 99%) and/or very noisy results. The same is true for the search window size and node spacing. Uncorrelated areas will be left blank in the outputs. Furthermore, the code allows to set up a post-processing filter to smooth the outputs (cfr. chapter 2, section 2.5.3.5).
Figure 2.9: Explanation of the steps operated by 3D-DIC in order to get full displacements fields, and the strain invariants. After definition of a correlation window (green) and a search window (red), the vector displacement field is calculated. From this, through a continuum hypothesis, the full 3D strain tensor field is calculated, and therefore the maximum shear and volumetric strains values. The images refer to the outputs for the sample NaCl-biotite, loaded at 6.64 MPa after 44.5 hours compaction and 21% vertical shortening.
To be able to characterize microfabrics in 4D (three dimensions and strain), sµCT was added to a sophisticated suite of classical methods that includes light microscopy, SEM, EPMA and EBSD. Each of these techniques delivers specific information (Table 2.1), which combined together with sµCT allow the full characterization of samples in 4-dimensions. The 2D analysis were in fact conducted on the actual tomography samples, this allows extrapolation of 2D information to the 3rd dimension (and to the 4th dimension, strain).

<table>
<thead>
<tr>
<th>Analytical technique</th>
<th>Acquired information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Microscope</td>
<td>Mineralogy and Microfabrics</td>
</tr>
<tr>
<td>SEM and EDS</td>
<td>High resolution mineral associations</td>
</tr>
<tr>
<td></td>
<td>Major element distribution</td>
</tr>
<tr>
<td>EPMA</td>
<td>Chemical Compositions</td>
</tr>
<tr>
<td>EBSD</td>
<td>Orientation</td>
</tr>
<tr>
<td></td>
<td>Microfabrics</td>
</tr>
</tbody>
</table>

Table 2.1: Tabulation of the informations acquired for each 2D analytical technique.

2.4.1 Data acquisition

2.4.1.1 Samples and samples preparation

From a hand specimen that covers the margin of an eclogite shear zone, four 2-mm thick rock wafers covering the strain gradient were extracted in x-z kinematic orientations. From these wafers, subsets with dimensions of 2 x 2 x 6 mm were cut for sµCT. The wafers including the sµCT samples were then polished into thin sections that could be used for further analyses using light microscopy, SEM, EPMA and EBSD (Figure 2.10).

2.4.1.2 sµCT

X-ray absorption microtomographic data were collected at the beamline 2-BM of the Advanced Photon Source (APS) of the Argonne National Laboratory, Chicago, USA, using a monochromatic beam of 27 keV and a low sample-detector distance to minimise phase contrast.

To ground-truth the intensity values of the sµCT data, the X-ray attenuation
coefficients for the mineral phases have been calculated from the chemical composition obtained through EPMA analysis, following the procedure outlined in section 2.2.4.1. Averaged electron microprobe analyses were used to calculate the X-ray attenuation coefficients for increasing energies. To correlate the chemical compositions to the tomography data, the chosen energy was 27 keV, which corresponds to the energy of the synchrotron experiment. Figure 2.11 compares the calculated absorptions with three grey value histograms from the three studied datasets and it allows identifying some of the metamorphic processes that affected the sample. For example, the peak for plagioclase, which is clearly present in the low strain dataset, is replaced by a minimum in the high strain domain, reflecting the lack (or a very small presence) of plagioclase in the eclogitic shear zone centre. This analytical strategy, where the actual microtomography sample was polished...
2.4 Part I: Natural samples from Kråkeneset, Western Gneiss Region (Norway)

and used for electron microscopy and EPMA analyses, allowed the combination of compositional measurements with intensity signals and thereby anchor the two X-axes against each other (see also subsubsection 2.4.3.4).

Figure 2.11: The graph shows grey value histograms calculated from three SuCT datasets in 32-bit floating point data. The calculated absorption coefficients ($\mu$) for the mineral phases correlate with grey scale values measured on the microtomographic data. The histograms reflect the metamorphic reactions during strain localisation. The peak at 0 value represents the atmospheric peak.

2.4.1.3 SEM/EDS/EPMA

Mineral assemblage and chemical zoning were analysed on the carbon-coated thin sections using a Zeiss SIGMA HD VP Field Emission SEM equipped with an Oxford Instruments SD EDS detector and AZtec software for acquisition and processing of EDS spectra, at the School of Geoscience in Edinburgh. Working conditions during acquisition of SEM backscatter images and during EDS analysis were 20 kV acceleration voltage and a working distance of 6.9 mm. Chemical compositions, to be correlated with the X-ray absorption coefficients, were measured on a Cameca SX100 electron microprobe at 20 kV acceleration voltage and a beam diameter of 3 µm, at the University of Edinburgh. The microprobe is composed by 5 vertical crystal spectrometers and a PGT Spirit energy dispersive analyser. Natural standards were used. Further microprobe analyses were acquired at the EMPA at the University
of Munster, using a JEOL 8530F electron microprobe. The standard microprobe conditions were 15 nA and 20 kV for quantitative analysis and 50 nA and 15 keV for the element mapping. Standards used for quantitative measurement were jadeite (Na), kyanite (Al), sanidine (K), olivine (Mg), hypersthene (Si), diopside (Ca), rhodocrosite (Mn), rutile (Ti), fayalite (Fe), and chromite (Cr). Compositional maps were obtained using XMapTools® v. 2.3.1 (Lanari et al., 2014).

2.4.1.4 EBSD

Crystalllographic orientations were measured on a Jeol 6610 SEM equipped with a NordlysNano EBSD detector (Oxford Instruments). Working conditions during acquisition of the EBSD patterns were 20 kV acceleration voltage, 70° sample tilt, high vacuum (in case of the carbon-coated samples 0617 and 066B2), and low vacuum (30 Pa, in case of the uncoated sample 0618). EBSD patterns were acquired on rectangular grids with step size varying from 0.8 to 4.8 µm. All thin sections were chemically polished with colloidal silica prior to EBSD analysis. EBSD patterns were indexed with the AZtec software (Oxford Instruments) and processed with Channel 5 software (Oxford Instruments). Raw EBSD data were processed to reduce data noise following the procedure tested by Prior et al. (2002) and Bestmann and Prior (2003).

2.4.1.5 Quant3D

Quant3D is a program for fabric analyses, developed by (Ketcham, 2005b) and by (Ketcham and Ryan, 2004), but it is based on concepts developed earlier. It is written in IDL programming language, and includes three main fabric analysis methods. Originally developed during previous works on two-dimensional analysis (Ketcham, 2005b and references therein), this method can now be used also to analyse 3D structures, as new imaging techniques such as µCT provide orthogonal sections at different angles of the sample. The Mean Intercept Length (MIL) is based on the mean distance between material interfaces in different orientations. For measurements relative to single phase fabrics, Quant3D also includes Star Volume Distribution (SVD) and Star Length Distribution (SLD). These analyses are calculated by placing star points inside the material of interest, and by measuring the distances of each point to the next material boundary. The distances are then normalised to calculate anisotropies in the sample. The software determines the eigenvectors (ù1, û2, û3) and eigenvalues (ò1, ò2, ò3) of the fabric tensors, which define orthogonal principal axes and are related to the moment of inertia, the degree of anisotropies (DA), the isotropy index I and the elongation index (E). The results can be visualized as a 3D rose diagram, where each vertex is projected from the unit sphere either inward or outward from the
2.4 Part I: Natural samples from Kråkeneset, Western Gneiss Region (Norway)

origin of the star points. The vertex positions from the origin are normalized by the maximum distance value. In the rose diagram, eigenvectors, scaled by their respective eigenvalues, are also plotted. The rose diagram can be visualized as rendered surface with a colour code mode, where the red colour represents a normalized value of 1.0, as a distance from the origin equal to the coordinate axis length: lower values, indicating closer distances to the origin, are represented with cooler rainbow colours (Ketcham and Ryan, 2004). The results can be exported in the VRML format, containing all the spatial informations and readable by lots of applications. The rose diagram can also be visualized as wire or points.

Figure 2.12: Left: The tomographic data are first segmented to extrapolate the material of interest. Simplified from Ketcham (2005b). Star points are placed within the segmented material: the distance of each star points to the next material boundary are calculated in many orientations and normalized, and plotted in rose diagrams (right). The rose diagram can help therefore to identify the main deformation fabric or shape fabrics. The represented rose diagram does not correspond to the image on the left.

2.4.2 Data processing

The reconstructed X-ray absorption microtomographic datasets were prepared for garnet segmentation. The contrast in the images was enhanced to facilitate the segmentation between garnet and the other mineral phases. The images were saved in Bitmap format (.bmp) in order to keep the new contrast. Data were then filtered using an Anisotropic Diffusion Filter 2D to reduce image noise (Tschumperle and Deriche, 2005; Schlüter et al., 2014). Using the image processing software ImageJ® (Schindelin et al., 2012), garnet was then segmented from the data using Statistical Region Merging followed by Global Thresholding (Nock and Nielsen, 2004). Figure 2.17 illustrates the workflow used to analyse these data.
2.4.2.1 SµCT data: reconstruction

1500 projections per dataset were reconstructed into 3-dimensional image stacks using the gridrec algorithm (Gualda and Rivers, 2006). The voxel side length of the reconstructed data is 1.3 µm. The reconstructed data were successively cropped, to remove as much background as possible, and avoid partial volume effects for the filtering and segmentation process.

2.4.2.2 SµCT data: filtering

**Anisotropic Diffusion Filter**

This filter is a common non-linear denoising filter implemented in ImageJ® (Perona and Malik, 1990), which smooths the image gradually, through a diffusion process, while preserving the edges. This process is modelled and iterated until it reaches the best solution to the equation. The best solution to the equation is verified through a visual check on the level of noise included in the histogram: the less noise the histogram, the better the solution. The diffusion stop criterion is set up manually by choosing the parameters $a_1$, $a_2$ and number of iterations. The parameters were chosen after repetitive attempts which did not provide a good filtering of the data. The more iterations, the smoother the image: eventually, the image will reach uniform intensity (Tschumperle and Deriche, 2005; Schlüter et al., 2014). The parameters I chose were as follows: 20 iterations, and $a_1$ and $a_2$ set up to 0.7 and 0.5 respectively. Before applying the filter, the contrast of the images was improved, and images saved as Bitmap format in order to keep the new contrast.

2.4.2.3 SµCT data: segmentation

**Statistical Region Merging (SRM)**

This algorithm is part of the ImageJ® plugins, and, as the name suggests, is a region growing technique, which groups homogeneous pixels together and grows them iteratively by merging other pixels or smaller regions. The limit of regions to be merged together is determined by a statistical test and the scale is controlled by the size of the chosen operator $Q$. The higher the value of $Q$, the higher the number of subregions permitted and the more detailed the resulting image. However, a more detailed image is also noisier (Nock and Nielsen, 2004) (Figure 2.13). The changes operated by SRM can be visualized in the image histograms. Each boundary phase is marked in the histogram by a vertical line, which allows global thresholding to segment the material of interest in a much more controlled way (Figure 2.13). In some cases, the choice of using one single output of SRM was insufficient as the algorithm may segment two phases together (e.g. olivine and garnet). In ImageJ®, it is possible
to combine different SRM outputs to obtain the best segmentation by using Image Calculator and Multiply and/or Subtract operator to get rid of unwanted segmented phases or islands. The Subtract operator was used in the low strain domain sample, to subtract olivine grains from garnet segmentation (Figure 2.14). Multiply operator was used in the more deformed samples to obtain a better and cleaner segmentation of garnet grains. This operator multiplies two binarised images and the output is a binarised image where only the pixels with values 1 in common between the two images are kept.

**Figure 2.13:** Image showing the results of Statistical Region Merging technique for increasing Q. Scale as in image A. A) Original data. B) SRM Q=2. C) SRM Q=10. D) SRM Q=25: note that the image is more detailed. E, F, G) Histograms relative to the three different SRM parameters: note the increasing vertical lines for increasing Q.

**Global Thresholding**

This method constitutes the simplest and most commonly applied approach to binarisation. A single grey scale value is chosen from the histogram to separate the regions of interest (Figure 2.15). Global thresholding can be subdivided into subcategories that can be selected by the user. Iassonov et al. (2009) and Schlüter et al. (2014) reviewed these categories.

**2.4.2.4 EBSD software**

Crystallographic data were plotted on pole figures as one point per grain. Pole figures are oriented with their horizontal diameter corresponding to the trace of the mylonitic foliation; the stretching lineation is parallel to the trace of the foliation. Crystallographic maps were produced to highlight phase distribution
Figure 2.14: Summary of the workflow followed in ImageJ® to segment the gabbros in Kråkeneset. A) Original image. B) Image filtered with Anisotropic Diffusion 2D. C) SRM Q=5 and corresponding histogram. D) SRM Q=100 and corresponding image. E) Segmented olivine from C). F) Segmented garnet and olivine from D. Due to the many details and level of noise, garnet cannot be segmented by its own. G) Output from the Subtract operator between F and E. Multiply operator was used in image with background in black, and phases in white. H) Final refined output.
2.4 Part I: Natural samples from Kråkeneset, Western Gneiss Region (Norway)

Figure 2.15: Image illustrating how global thresholding works in ImageJ®. The threshold values are chosen from the histogram (on the right) and their effect can be visualised on the image to the left in red colour (original image). The shown algorithm is the default option.

(Phase Map), the internal misorientation of grains (Local Misorientation Map) and the crystallographic orientation of grains with respect to specific direction of the kinematic reference frame (Inverse Pole Figure Map). On EBSD-derived maps, high-angle boundaries (grain boundaries, misorientation > 10°) and low-angle boundaries (subgrain boundaries, misorientation > 3°and < 10°) were indicated with black and fuchsia lines, respectively. Histograms of misorientation angle distribution for correlated and uncorrelated pairs of grains were also derived and compared with a theoretical random distribution (Wheeler et al., 2001).

2.4.3 Data analyses

2.4.3.1 Garnet volume

Garnet total volume was calculated from segmented data through the Volume fraction operator in ImageJ®. In microtomographic data, volume calculations are affected by errors introduced by the segmentation method (Arns et al., 2002). To estimate the errors, the method described in Fusseis et al. (2012) was used. Each segmented volume was both numerically eroded and dilated by 1 voxel, and the resulting changes to the volume and label analysis were quantified. The resulting quantifications are considered as maximum possible errors. Besides providing errors bars, binary data that have been eroded or dilated have the potential to reveal details on the shape and spatial arrangement of voxel clusters, as each morphological operation will cause voxel clusters to join, break up or disappear altogether (cfr. chapter 2,
onset in Figure 3.6). A version of the segmented garnet data that underwent a single morphological erosion step was analysed. Morphological erosion removes each voxel classified as garnet that is not completely surrounded by other voxels classified the same. The erosion operator responds to the size and shape of the voxel clusters, and the shortest diameter defines this response. The smallest unit that would survive a morphological erosion step is a cubic array consisting of 33 voxels. A much larger, spherical voxel cluster would retain its spherical shape through multiple erosion steps. Oblate voxel clusters, which are characterised by one radius being substantially shorter than others, will respond differently to erosion. Where cluster shapes are irregular, morphological erosion will strangulate clusters at the shortest diameters (e.g. the weakest links) and break them apart into several smaller ones, which is reflected by a corresponding change in the cluster size distribution.

2.4.3.2 Interconnectivity

Quantification of face-connected garnet volumes and grain sizes were performed in AvizoFire® (v.8) using its Labelling and Label Analysis operators, by selecting the neighbourhood at 6 (section 2.2.5). Since X-ray absorption microtomography does not detect grain boundaries in the garnet coronas, numerical separation of the voxel clusters into individual grains is impossible in these data and interpretation is restricted to voxel clusters. To avoid introducing numerical shape artefacts during the analyses of garnet, isolated voxel clusters with a volume smaller than 125 cubic voxels (5 x 5 x 5 voxels, 275 µm$^3$) were removed using the Analysis Filter operator (see Fusseis et al. (2012) for details).

2.4.3.3 Fabric and shape analysis: Quant3D

*Star Volume Distribution* can also be used to estimate the preferred shape orientation of garnet clusters in the material. If the star points are placed outside the material of interest, the distances to the next material boundary represent distances to the material of interest, and thus they give an indication of the shapes (see section 2.4.1.5). The input data need to be binarised again, converting them to 8-bit format with 255 levels of grey. The parameters were as follows:

- in Preferences, orientations were set to *Geological*;
- threshold values was set to 0-254. This threshold assigns value 0 to garnets, and value 1 to the background. To analyse garnet fabrics, the threshold should be set to -1-254 to assign value 1 to garnets and value 0 to the background.
2.4 Part I: Natural samples from Kråkeneset, Western Gneiss Region (Norway)

![Image of microtomographic datasets: low strain (left), intermediate strain (middle), and high strain (right). Mineral phases and features are recognizable from the corresponding SEM images (Figure 3.2).]

**Figure 2.16:** Microtomographic datasets: low strain (left), intermediate strain (middle), and high strain (right). Mineral phases and features are recognizable from the corresponding SEM images (Figure 3.2).

**Figure 2.17:** Image analysis workflow used to analyze Kråkeneset gabbros.

- the option "Generate orientations" was checked and Random orientations and Dense vectors chosen. These were default values.

2.4.3.4 Data integration from multiple sources

Using AvizoFire, the 2-dimensional electron backscatter images together with the EDS and EBSD image data were reintroduced into 3-dimensional space to combine observations from various sources into multidimensional datasets (Figure 2.16). This allowed correlation of X-ray absorption signals with chemical compositions and crystallographic information and, as a result, extrapolation of observations made in two dimensions to the third dimension.
2.5 Part II: Experimental deformation of NaCl

Uniaxial compaction experiments to study pressure-solution processes in NaCl were performed in custom made X-ray transparent presses, that were designed and built at the University of Edinburgh, School of Geosciences’ Mechanical workshop. Evolution of porosity and increasing deformation of the sample were monitored by scanning the presses at regular interval times at the X-ray microtomograph in Edinburgh. Volumetric DIC was then applied on increasingly deformed datasets, to calculate maximum shear and volumetric strains, and strain rates for each sample (section 2.3).

2.5.1 Experimental methods and data acquisition

2.5.1.1 Cell design

The experimental cells are composed of a top piston and lower chamber made from PEEK (Polyether-ether-ketone), hosting 5 mm diameter samples (Figure 2.18). Top piston and lower chamber were machined to a tight slip fit and Brasso\textsuperscript{TM} was used to hone the piston and chamber together to provide a smooth slip fit with minimal stiction. High-vacuum silicone grease was used to provide a seal in a very narrow annulus between top piston and lower chamber. Loading frames, composed of two 20 mm thick Perspex plates joined by three steel legs (M5 threaded rod) allow a pneumatic actuator, moved by compressed air at 60 psi, to apply a constant uniaxial load on the samples (Figure 2.19). Choke valves (made by Legris LtD) were used as shut-off valves for the air flow. Moreover, as they open slowly, the force from the pneumatic actuator can be reapplied in a controlled way without shock loading of the sample. Saturation of the samples was assured by positioning a fluid reservoir $\sim 40$ cm above the base of the cells.
2.5 Part II: Experimental deformation of NaCl

Figure 2.18: Illustration showing the different components of the experimental setup: A) Top piston and cross-sectional view (red dashed line); B) Lower chamber and cross-sectional view of the base (red dashed line); C) Schematic sketch illustrating the position of the sample vessel, within the frame, the position of the pneumatic actuator, and the fluid reservoir. Pneumatic actuator, 25 mm bore (435-8870, from RS-online website http://uk.rs-online.com/web/p/products/). Scale in figures.
2.5.1.2 Sample preparation

NaCl (Fisher Scientific, analytical reagent) was sieved to 250-300 µm grain size to create a granular sample. Different sample powder mixtures, and two different uniaxial loads were applied, to study their effects on pressure-solution processes. Sample mass was chosen in order to accommodate a 7 mm height sample. Initial porosity was calculated to be 39.75% in the pure NaCl samples. To assure sealing, the piston was firstly pushed into the lower chamber for about 1 mm length, gently rotated to allow the grease to spread homogeneously, and then pushed again until it reached the sample: this way, a homogeneous layer of grease will be created where the piston enters the cell and which will seal the cell.

2.5.1.3 Material test

Trial experiments were conducted in order to test different sample mixtures, and their response to the loading conditions. Pressure-solution processes are recognized to be favoured in the presence of clays and phyllosilicates (Spiers et al., 1990; Bos et al., 2000b) or platy minerals. On this base, kaolinite clusters, sieved at 150 µm, were mixed with NaCl grains, to monitor the evolution of the process in time. Unfortunately, even though the compaction rates are accelerated in the presence of kaolinite, the grain size was too small to be able to identify in the microtomography data, as well as there was insufficient contrast compared to NaCl grains. Tests with biotite, kaolinite and muscovite mixtures were performed at different energy conditions, and mixed with NaCl grains and brine solution.
• Kaolinite was immediately recognized as unsuitable, as it appears virtually indistinguishable from the brine and therefore it cannot be separated from the brine and its behaviour cannot be monitored over time (Figure 2.20).

• Muscovite and biotite grains appeared to be quite bright in the tomography data, and recognizable from the other phases. Biotite, at 70 kV energy, proved to be the most suitable for our experiment, due to a slightly higher content in iron and consequently a brighter signal in the data. However, as the sample compacted, the grain size proved to be too small to ensure enough contrast: for this reason, in the third experiment, the grain size changed from < 180 µm to 180-212 µm.

• Image analysis proved to be difficult even in the presence of biotite grains: even though visual inspection of the data allows the biotite to be distinguished, no segmentation algorithm was able to separate the phyllosilicate grains, and as compaction increases, the contrast between biotite and NaCl is progressively reduced.

In the last experiments, flakes of biotite were used instead of sieved grains: flakes were obtained by simply cutting mica sheets finely using a scalpel, perpendicular to the basal cleavage. In this way, a platy mineral was obtained, thick enough to be recognized and monitored over time in the microtomographic images. The presence of phyllosilicates acts as a heterogeneity, helping to localise the pressure-solution process (Spiers et al., 1990; Bos et al., 2000b).

Similarly, I wanted to test the effect of a harder structural heterogeneity on the process, to see if it assists creating strain caps. Various test materials were chosen (calcite, fluorite, garnet), all very bright and clearly recognizable in the data. However, glass beads (diameter 0.5 mm) were instead chosen: the rounded shape makes this material easy to recognize by shape even at the highest degree of compaction (Figure 2.20 C).

2.5.1.4 Experimental setup

Samples were initially loaded dry for 10 minutes (except for last two experiments where I used a wet loading method), to produce a starting aggregated material, then flooded with saturated NaCl solution and re-loaded to the desired pressure to reach a constant uniaxial load. The wet loading method was as follows: 1) inlet fluid connection was open to allow some brine sitting at the bottom of the piston; 2) a slurry of NaCl and glass beads was created and carefully introduced into the vessel, with the help of a pipette and the excess liquid removed; 3) top piston was placed. In
the NaCl and biotite sample, the same preparation was followed, with the exception that the biotite was concentrated between two layers of NaCl grains, in addition to the filter paper sheets, to avoid clogging of the biotite particles. A smaller and a bigger uniaxial load (respectively, 1.66 MPa and 6.64 MPa) were applied by means of pneumatic actuators of different internal diameters: 10 mm and 20 mm, respectively (Figure 2.18). Scans were taken at regular intervals to monitor the evolution of porosity and deformation of the samples. For each scan, the press was first unloaded: the chock valves were closed, and the air cable disconnected from the valve which allowed the pneumatic actuator to unload the sample. The press was then positioned in the rotary stage of the X-ray tomograph (see section 2.2) and scanned. The duration of each scan was roughly 67 minutes. After each scan, the press was re-loaded to the desired pressure and the sample was left to compact till the next scan. Compaction curves for
2.5 Part II: Experimental deformation of NaCl

each sample, showing the compaction duration and the number of scans are reported in chapter 4.

2.5.1.5 µCT scanning parameters

The CT scanner in Edinburgh has a cone-beam geometry (final angle of rotation 360°), and it is composed of:

1. X-ray head source in transmission mode: Feinfocus dual transmission/ reflection, for high resolution/brightness respectively. It can operate from 10 to 160 kV;

2. camera: Perkin-Elmer XRD0822 amorphous silicon 20 cm flat panel detector, with a terium doped gadolinium oxy-sulfide scintillator (camera pixel size is 0.2 mm);

3. ultra high precision rotary air bearing stage (MICOS UPR-160-AIR).

The control software was programmed in-house. The target power used was 2.8 W; however for practical image quality reasons, the X-ray energy, acquired projections and exposure time changed between the experiments, and the working conditions for each experiment are described in chapter 4 (section 4.4).

Data were reconstructed using Octopus® software (Dierick et al., 2004), which uses a filtered back-projection algorithm (see section 2.2.3).

2.5.1.6 SEM

Samples were recovered from the X-ray transparent presses at the end of the experiments to be imaged at the SEM facility in the School of Geosciences, in Edinburgh, and to assess the type of microstructures developed during the experiments. Sample were gold coated in order to be imaged using secondary electrons, and the energy used was 10 kV.

2.5.1.7 Volumetric Digital Image Correlation: 3D-DIC

Misalignments in x and y, and misorientation > 5°can introduce errors in the outputs of the correlation (Dr. Erika Tudisco pers. comm.). To avoid this, two punch holes were indented on the base of the lower chamber: these holes, together with the central fluid bore hole, define the orientation of the sample and therefore of the µCT datasets. 3D-DIC on the acquired datasets was performed using TomoWarp2, developed at Lund University in collaboration with Laboratoire 3SR of Grenoble University (Tudisco et al., 2015).
Preliminaries  In order to run TomoWarp2 successfully, some preliminaries need to be followed:

- Reconstructed datasets to be correlated can be either a list of 2D raws or a 3D raw. The program works also with tiffs, but in the version I used there was a bug. In order to have the right type, images were imported in ImageJ® and converted to 16-bit raws and saved as Image sequence.

- The datasets also have to be little-endian type order: this can be easily checked in ImageJ®, from the menu bar Edit ⇒ Options ⇒ Input/output (Figure 2.21). Images that were not little-endian type order were converted. When the conversion is not possible, the graphic interface of the code allows to deselect the little-endian type order when uploading the input data (Figure 2.21).

- The datasets cannot be rotated or translated with respect to each other. As mentioned above, the indentations on the lower chamber allowed to reconstruct the orientations of the dataset. I applied the Rotate operator in ImageJ® on the misoriented datasets. Misalignments in x and y were calibrated and correct using the Translate operator in ImageJ®.

- Application of a denoising filter.

- Application of a denoising filter.

- As option, datasets can also be cropped, to remove as much background as possible, and filtered for noise to improve the quality of the results. If the background results to be a problem (not very well correlated datasets or correlation values very low), it is sensible to apply a mask in ImageJ® (not necessary in these data).

- The input data to be correlated need to have the same name/prefix and file name format type or the program will not recognize the two datasets to be correlated.

Code setup   The chosen parameters for my analyses were defined on the basis of grain size, and compaction curve, and through some tests. The graphic interface (GUI) of the program allows setting the parameters: input data, output name folder, output directory, type of data, search window, correlation window, node spacing. Other optional parameters can indicate a region of interest within the datasets (not used in these data). The correlation coefficient should be set up as percentage. In the post process tab menu, the strain mode and the filters can be chosen: the mode strain was chose large, and a kinematic filter with kernel size 3 was applied to smooth the outputs. Once the parameters have been chosen, the GUI allows saving the file as text file. The text file was then imported in a bash shell script, which I created and used to run the
2.5 Part II: Experimental deformation of NaCl

program through Python® v. 2.7 on the Terracorrelator cluster. The Terracorrelator cluster is a super-computer facility at the University of Edinburgh, which allows to run programs demanding high computational power (see Appendix A).

![Image of Tomowarp2 interface]

**Figure 2.21:** Graphic interface of Tomowarp2.

2.5.2 Data processing

The reconstructed datasets were processed for image analysis using AvizoFire® v.8.1 and Avizo® v.9 following the workflow explained in the following sections and illustrated in Figure 2.27.

2.5.2.1 µCT data: filtering

Microtomographic data were pre-processed for denoising through Remove outliers and Median Filter. **Remove Outliers** "corrects" the image by replacing the pixels with a median value from the surrounding neighbourhoods (radius) if the pixels deviate from the median by more than a specific value, indicated by the threshold. It removes the "salt and pepper" effect of the image. **Median Filter** is a non-linear ranking filter, in which median values are calculated from the neighbour pixels, without the influence of extreme values. It smooths the image with a cubic kernel, while preserving the edges (or with minimal modification of the edges). The size of the radius (or kernel) determines the smoothness of the image: the bigger the kernel size, the smoother the image, but details can be lost (Figure 2.22). Median filter was used to denoise images.
from the CT experiments, in combination with remove outliers filters, as the CPU time needed for this operation is much lower than the Anisotropic Diffusion filter.

![Figure 2.22: Outputs of different denoising filters: A) Original image; B) Remove outliers C) Median filter, kernel size=2; D) Anisotropic Diffusion Filter 2D, 15 iteration, a_1=0.5, a_2=0.7;](image)

2.5.2.2 \( \mu \text{CT data: segmentation} \)

Before segmentation, data were cropped to cubic datasets of 400\(^3\) (17.6 mm\(^3\)), from centre regions of the reconstructed CT data, on which porosity analyses were performed. Data were then segmented through Interactive Thresholding (Figure 2.23). This algorithm allows threshold to be selected interactively: the current selection, chosen from the histogram, is displayed as an orthoslice representation with grey-scale data as background, and whose orientation can be chosen (Figure 2.23). The selected labels can be shown in 2D and 3D. Although being less automated, this segmentation method allows to carefully select threshold values, check them in 3D, resulting in a much faster segmentation.

2.5.2.3 \( \mu \text{CT data: labelling} \)

The segmented data were then labelled through the Labelling operator in AvizoFire\(^\circledR\) v.8 and Avizo\(^\circledR\) v. 9 (see section 2.2.5). In all analyses, the chosen neighbourhood was 6 and it was kept constant across different samples and across increasingly shortened datasets.
2.5 Part II: Experimental deformation of NaCl

2.5.2.4 µCT data: separation

Separation in pores and throats was achieved using the Separate Objects operator in Avizo (Figure 2.25, Figure 2.27). This algorithm is a watershed segmentation of a distance map of the binarised data, implemented natively in Avizo. Watershed algorithm is part of the local adaptive segmentation methods, which take into accounts neighbourhood characteristics (Schlüter et al., 2014). This algorithm is a region flooding segmentation method, which expands the marker regions accordingly to priority maps in which seeds are identified (H-maxima or distance map) until the flooding region reaches the watershed lines (Figure 2.24 A). The priority map is a grey scale image as height or altitude map. In the case of Separate Objects, the priority map is a chamfer distance map, in which the maxima regions, labelled, represent the marker regions thus the seeds. In the case of Watershed algorithm, a gradient map is created, which represents the gradient between the phases to be segmented. The same procedure can be completed step by step following the tutorial explained in AvizoFire® manual and by applying the module H-maxima as distance map. H-maxima is an image representing the areas with the highest altitude, and thus the seeds. The numbers of separated objects, and therefore throats, is controlled by the number of labelled markers (Figure 2.24 B, C and Figure 2.25). The watershed lines are then computed by reversing the distance map and on the basis of the binarised input image in order to create "valleys": the watershed lines represent the crest lines between the valleys (Figure 2.24).

Although Separation Object is based on watershed segmentation, the outputs are clearly different. I tested different input parameters and the resulting binarised data on grain separation. Figure 2.26 represents the number of individual particles after

![Image of interactive thresholding on pore space rendered in red colour.](image)

**Figure 2.23:** Interactive thresholding on pore space rendered in red colour. On the right the settings in AvizoFire are shown.
Figure 2.24: Results of “Separated Objects” operator in AvizoFire®, based on the definition of pore throat: A) Sketch of seeds, valleys and watershed lines computing during the separation. B) XY plane, different colours indicate different pores. C) 3D viewer through surface rendering of the separated pores.

Figure 2.25: Sketch illustrating the effects of separation for a connected and disconnected pore space. In the case of a disconnected pore space, the throat does not exist and pores are identified with separate labels.

applying segmentation, separation and label analysis. I tested two different separation algorithms, in order to verify the effects on volume calculations, choosing parameters
which identify grains more or less compacted: a marker extent (or H-maxima) equal to 1 would separate the grains in the least compacted way, creating more boundaries between grains; on the contrary, if H-maxima is set to 4, it will keep grains less separated. The particles are clearly very sensitive to the segmentation and separation algorithm used, and therefore cannot be properly analysed in order to monitor the degree of compaction over time. In fact, although grains can be distinguished in all the slices, as compaction increases, they start to indent each other, impeding a good automated and consistent separation of the grains. This problem is not present in the separation of pores, as pore-throats space, for which a constant marker equal to 1 (most separated) was chosen and kept constant with Separated Objects, through time steps, providing a consistent workflow for the segmentation of pressure-solution data. This is the reason why the analysis of the microtomographic data focused on the evolution of the porosity as a function of time, leaving the characterization of NaCl grains to a purely visual identification. The choice of Separated objects is also justified by the fact that Watershed segmentation will create under-segmented pores, introducing errors in the calculations, the Separate Object tool acts on the basis of a distance map and it leads to similar watershed segmentation but with improved results in 3D (Figure 2.24 C). The parameters for Separate Objects were kept the same in all analysed datasets: neighbourhood 6, with marker extent equal to 1, to represent the least connected pores.

![Graph showing the evolution of number of voxel clusters in relation to different separation algorithms inputs and for three compaction datasets (indicated by the amount of vertical shortening in [%]).](image)

**Figure 2.26:** Graph showing the evolution of number of voxel clusters in relation to different separation algorithms inputs and for three compaction datasets (indicated by the amount of vertical shortening in [%]).
2.5.3 Data analyses

Data analyses were performed on the samples loaded at 6.64 MPa, as these samples show a stronger evolution of the pore space.

2.5.3.1 Vertical shortening

For each sample, the vertical shortening was plotted as a function of time. The uniaxial shortening of the samples was calculated from vertical µCT slices: the height of the samples was measured from the vertical slices for each microtomographic scan, and the relative shortening, in percentage, was calculated through \( \epsilon_t = \frac{x_0 - x_t}{x_0} \) where \( x_0 \) represents the initial height of the sample, and \( x_t \) represents the height after a certain amount of time and compaction.

2.5.3.2 Bulk porosity

Bulk porosity analyses were performed through the Volume Fraction operator. Morphological erosion and dilation by one cubic voxel was performed, and corresponding data measured, following the procedure described in Fusseis et al. (2012) and in section 2.4.3. These data constitute the error bars in the volume quantification.

2.5.3.3 Pore size and shape

Label Analysis was used to characterise and quantify pore shapes and orientations (cfr. 2.2.5). The chosen neighbourhood was 26, as the labels had already been identified as least interconnected through the separation process (cfr. section 2.5.2.4). For the pore size distribution quantifications, pores with a volume smaller than 10 voxels were discarded from the analysis. A volume of 125 voxel corresponds to a pore with dimensions 5 x 5 x 5, and to a volume of 34328 µm\(^3\) assuming 6.5 µm as voxel size: this volume is rather big for a pore. On the contrary, a cubic volume of 10 voxels has dimensions 2 x 2 x 2.5, and corresponds to 2746.25 µm\(^3\). A comparison between different threshold reveals that a large amount of small sizes have been cut off where 125 was chosen as lower threshold, loosing therefore important information that might be related to microporosity or pores being chopped off with increasing compaction (see chapter 4, section 4.6.8). However, the overall trend is maintained across increasingly shortened datasets.

Absolute frequency were calculated in bins derived by the power of two. Pore size distributions were chosen to be represented volumetrically, as the morphologies of the objects can be directly observed in µCT data, therefore volume is a much more
meaningful measure than equivalent radius used in petrophysics (Anovitz and Cole, 2015; Emmanuel et al., 2015).

When considering shape and orientation analysis, 2 x 2 x 2.5 voxels is a meaningless volume to indicate any change in shape or orientation. On the other side, 125 voxels is too large. I chose therefore a limit lower threshold of 64 voxels (4 x 4 x 4) to analyse shape and orientation changes across the experiments.

Shape changes were analysed by plotting the eigenvalues of the pores inscribed ellipses in Flynn diagrams. Orientation changes were analysed by plotting the eigenvectors of the pores inscribed ellipses in equal area stereonets. Orientation plots were obtained using Stereonet® v.9 (Allmendinger et al., 2011): pores were plotted as poles to planes, representing the longest diameter of the pores and whose theta (θ) and phi (φ) angles were determined in Avizo® v.9.

2.5.3.4 Interconnectivity

Interconnectivity analyses were performed on labelled data. Analyses were also performed on eroded data, to check the influence of possible segmentation errors (see section 2.4.3).

Label analysis The interconnected pore clusters were successively analysed through the Label analysis operator in Avizo®, to quantify their volume and volume fraction with respect to the total amount of pore space in the subvolume (see section 2.2.5).

Skeleton analysis The complex 3D structure of the pore space does not allow an understanding of the internal morphology of pores and connectivity. Skeletonisation is becoming a very powerful tool to analyse complex 3D morphologies. The algorithm is based on the concept that any volume of an object can be represented by a one-dimensional segment located at its geometrical middle, thus defining the medial axis of the object (Lindquist et al., 1996). The algorithm reduces a 3D network of voids into a group of 1-dimensional segments, connected to each others by nodes. The medial axis of a 3D network is represented as a surface. To obtain this, the algorithm progressively thinness the segmented data from a distance map to obtain a single central lines of pixels (segment). Each pore constitutes a single skeleton, made up of segments and nodes: disconnected pores, based on the distance map, will be represented as separate skeletons. The length of each segment is proportional to the length of each pore. An estimate of the minimum thickness of each segment is instead computed by a re-dilation step on the distance map. This way, while segments and nodes retain the topological information (e.g. interconnectivity), they loose the geometrical information (Lindquist et al., 1996). The skeletons can however
be quantified and characterised in three dimensions, through the number of segments, nodes, the number of segments attached to each node (coordination number), the thickness of each segment and the volume of each skeleton (which does not represent the volume of the pore).

Skeletonization was performed in increasingly shortened datasets on segmented data using the *Auto-skeletonisation* operator in Avizo® v.9 using default parameters. The characteristics for each skeleton are obtained through the *Spatial Graph* operator. In the analyses, the number of connected skeletons was plotted against the number of segments per skeleton for increasingly shortened datasets as a measure of connectivity evolution with increasing deformation and time.

2.5.3.5 Strain analysis

Results of 3D-DIC (volumetric Digital Image Correlation) are represented as vertical slices through the middle of the samples for progressively shortened datasets. The vertical slices were obtained by re-slicing the outputs of the maximum shear and volumetric strain through the *Reslice* operator in ImageJ® with default values. Colours for the output images have been assigned as follows: for the maximum shear strain, a fire colour look up table (LUT) was applied (warmer colours represent higher values of strain); for the volumetric strain, a yellow LUT was chosen, to differentiate it from the maximum shear strain field. In this colour table, darker colours represent negative values, indicative of compressional field. Values of the 3D-DIC were then divided by the time steps to calculate strain rates (s\(^{-1}\)). The images were then re-mapped to indicate strain rates.

2.5.3.6 Microstructural analysis

The interfaces between NaCl grains, and with other materials (phyllosilicates and glass beads) were closely imaged to investigate the type of microstructures developed during the experiments, and to gain new insights into the PSC process.
Figure 2.27: Figure illustrating the image analysis workflow applied on the pressure-solution experimental data. 1. Original image. 2. Filtered image after applying Median filter, kernel size equal to 2. 3. Segmented image through Interactive thresholding. The data are then analysed for bulk porosity through the Volume Fraction operator. Erosion and dilation of the data allowed for estimating errors introduced by the segmentation. 4. Labelling of the segmented data for interconnectivity analysis. Note the only red pore at the bottom, disconnected from the main pore space. Erosion of the data is performed and labelling is recalculated. 5. Separation of the segmented pores in pores and throats, through Separation object operator, and subsequent Label Analysis on the individual pores. 6. Interconnectivity analyses are then performed on the labelled data visually and through Label Analysis of the interconnected pores: the same step is performed again on eroded data. 7. Skeletonisation on segmented data.
ABSTRACT

Reaction and deformation microfabrics provide key information to understand the thermodynamic and kinetic controls of tectono-metamorphic processes. However they are usually analysed in two dimensions, omitting important information regarding the third spatial dimension. Synchrotron-based x-ray microtomography was applied to document the evolution of a pristine olivine gabbro into a deformed omphacite-garnet eclogite in four dimensions, where the 4th dimension is represented by the degree of strain. The spatial transformation of garnet coronas into elongated clusters of garnets with increasing strain was investigated in rock samples, which cover a strain gradient into a shear zone from the Western Gneiss Region (Norway). The microtomographic data allowed quantification of garnet volume, shape and spatial arrangement evolution with increasing strain. These data were combined with light microscope- and backscatter electron images as well as electron microprobe-(EMPA) and electron backscatter diffraction (EBSD) analysis to correlate mineral
composition and orientation data with the x-ray absorption signal of the same mineral grains. With increasing deformation, the garnet volume almost triples. In the low strain domain, garnets form a well interconnected large garnet aggregate that develops throughout the entire sample. Garnet coronas in the gabbros never completely encapsulate olivine grains. In the most highly deformed eclogites, the oblate shapes of garnets reflect a deformational origin of the microfabrics. These oblate garnets direct synkinematic fluid flow and consequently influence the transport of dissolved chemical components. EBSD analyses reveal that garnet show a near-random crystal preferred orientation that testifies no evidence for crystal plasticity. There is, however, evidence for minor fracturing, neo-nucleation and overgrowth. Microprobe chemical analysis revealed that garnet compositions progressively equilibrate to eclogite facies, becoming more almandine-rich. These observations point to a mechanical disintegration of the garnet coronas during strain localisation, and their rearrangement into individual garnet clusters through a combination of garnet coalescence and overgrowth while the rock was deforming.

Author Contributions: This chapter has been submitted as paper contribution to the Journal of Metamorphic Geology. Microtomographic data were acquired at the Advanced Photon Source in Chicago by my supervisor Dr. Florian Fusseis and by Dr. Xianghui Xiao. Analyses of microtomographic data were conducted by myself: these included denoising and segmentation of garnet grains, interconnectivity and garnet size distribution analyses. I also correlated the signal of the microtomographic data with the chemical compositions obtained from the electron microprobe analyses. EBSD data were acquired at Plymouth university by Dr. Luca Menegon. Electron microprobe compositions to determine zoning in the garnets have been acquired by Dr. Stephen Centrella, at the University of Münster. Combination of these with the microtomographic results was performed by myself, in order to interpret the deformation history of the rock.
Chapter 3. The morphological evolution of garnet grains

3.1 Introduction

Synkinematic reaction microfabrics carry important information on the kinetics, timing, and mechanics of tectono-metamorphic processes. The spatial arrangement of reaction products reflects directions and magnitudes of mass and element transport. An assessment of the geometry of reaction microfabrics is therefore a critical component in reconstructing the tectono-metamorphic evolution of a rock. Despite being routinely interpreted in metamorphic and structural studies, reaction and deformation microfabrics are usually described in two dimensions, which can lead to incorrect petrographic and structural interpretations. In this study, garnet is used to explore the significance of a 3-dimensional approach to the description of synkinematic reactions and deformation microfabrics.

In nature, garnet represents an extremely versatile recorder of metamorphism (Baxter and Scherer, 2013) and in particular garnet coronas capture metamorphic processes “in flagranti” (Carlson and Johnson, 1991; Carlson, 2011; Ague and Carlson, 2013). Consequently, garnet coronas and their metamorphic significance have been intensely studied over the past decades (Mørk, 1985; Johnson and Carlson, 1990; Johnson, 1993; Spiess et al., 2001; Prior et al., 2002; Konrad-Schmolke et al., 2005; Massey et al., 2011; Goergen and Whitney, 2012).

Garnet porphyroblasts often hold the key to unravelling the synkinematic PT\(q\) conditions. The origin of these garnet porphyroblasts has been controversially discussed as either being evidence of rotational strains (“Snowball garnets”, Johnson (1993) and Jiang and Williams (2004)), as documenting strain partitioning (Bell and Johnson, 1989; Aerden, 2005) or, where polycrystalline, as forming from the coalescence of nuclei (Spiess et al., 2001; Dobbs et al., 2003).

Garnet also readily partakes in mylonitic deformation: crystal plastic deformation of garnets at lower crustal conditions was documented by, e.g., Ji and Martignole (1994, 1996), Prior et al. (2002), Storey and Prior (2005), Massey et al. (2011), and Martelat et al. (2012). Garnets in mylonitic eclogites from SW Norway were shown to have deformed by grain-boundary diffusion creep and by pressure-solution (Smit et al., 2011). However, garnet in eclogitic mylonitized micaschists was also shown to have deformed by cataclasis and frictional sliding (Trepmann and Stöckhert, 2002).

Conclusions derived in these studies often invoke an extrapolation from the second to the third spatial dimension, which is naturally speculative. With the advent of x-ray microtomography, garnet became the focus of a number of microstructural studies that explored the third spatial dimension (Denison and Carlson, 1997; Ketcham, 2005b; Whitney et al., 2008; Goergen and Whitney, 2012).
3.1 Introduction

These pioneering 3-dimensional studies outlined the possibilities that the combination of x-ray microtomographic data with other microanalytical techniques holds in regards to the interrogation of tectono-metamorphic processes. In this present contribution, I apply this approach to analyse the distribution of garnet in rock samples from Kråkeneset, a tectonic domain within the well-studied Western Gneiss Region (Norway) (Mørk, 1985, 1986; Austrheim, 1987; Boundy et al., 1992; Austrheim et al., 1997; Krabbendam and Dewey, 1998; Cuthbert et al., 2000; Engvik et al., 2000; Krabbendam et al., 2000; Engvik et al., 2001; Wain et al., 2001; Labrousse et al., 2004; Terry and Heidelbach, 2006; John et al., 2009; Hacker et al., 2010; Labrousse et al., 2010). There, fluid infiltration along precursory fractures led to the eclogitization and coeval mylonitic overprint of gabbroic rocks (Mørk, 1985; Austrheim et al., 1997; Krabbendam et al., 2000; Engvik et al., 2001; Lund and Austrheim, 2003; John et al., 2009; Müller, 2013). The field location is a gabbroic body in which hydrous eclogite-facies shear zones cross cut the almost pristine magmatic rock. There, reaction textures indicate that the eclogite-facies overprint is caused by the ingress of reactive fluids that helped to overcome sluggish reaction kinetics (Austrheim, 1987; Krabbendam et al., 2000; Lund and Austrheim, 2003; John et al., 2009; Müller, 2013). The rock samples cover a strain gradient ($4^{th}$ dimension) into a dm-scale mylonitic shear zone and document the metamorphic overprint. The strain gradient along the shear zones is ideally suited for such a study, in that it shows progressive deformation localization under well constrained P-T-fluids conditions. Based on the assumption that the strain gradient can be regarded as a proxy for time, which is a common assumption where strain softening leads to progressive strain localisation (Means, 1995; Fusseis et al., 2006; Fusseis and Handy, 2008), the samples allow characterization the spatio-temporal evolution of a gabbro into a deformed eclogite. In the samples, this transition is reflected by the evolving 3-dimensional distribution of garnets in the microfabric. The evolution of garnet, from its arrangement in a primary coronitic texture to forming a key component of the tectonic microfabric, was determined. To do this, a methodological workflow, that combined classical electron-beam techniques with Synchrotron x-ray microtomography, was developed. In combination, these data allow the speculation on the mechanisms that accomplished the transformation of garnet microfabrics.
Chapter 3. The morphological evolution of garnet grains

3.2 Geological Setting of the WGR

The studied rock samples come from Kråkeneset in the Western Gneiss Region (WGR) of the Norwegian Caledonides. As many other parts of this lowest tectonic unit in the Scandinavian terrains, the outcrops in Kråkeneset preserve evidence for Caledonian high-pressure metamorphism in association with the subduction of Baltica underneath Laurentia after the Silurian closure of the Iapetus ocean (Engvik et al., 2000; Krabbendam et al., 2000; Wain et al., 2001; Lund and Austrheim, 2003; Labrousse et al., 2004; John et al., 2009; Müller, 2013). It is commonly accepted that even though some of the rocks in the WGR were subducted to depths beyond 100 km, large parts of the complex remained metastable until fluid infiltration along brittle fractures and cleavage planes overcame sluggish reaction kinetics and initiated large-scale eclogitisation (Austrheim, 1987; Krabbendam et al., 2000; Wain et al., 2001; Labrousse et al., 2010). In Kråkeneset, the high-pressure metamorphic overprint takes the form of hydrous eclogites that occur within shear zones cutting dry gabbroic host rocks (Krabbendam et al., 2000; Lund and Austrheim, 2003; John et al., 2009). The pristine gabbroic mineral assemblage is preserved in the less deformed areas, and is characterized by an ophitic texture, in which garnet and orthopyroxene coronas surround olivine cores. Previous authors have interpreted these coronas as having derived from diffusion-controlled reactions of olivine and plagioclase (Mørk, 1985; Johnson and Carlson, 1990). The eclogite-facies mineral assemblages occur within narrow shear zones where, across their margin, a gradient from a “dry” gabbroic mineral assemblage (Ol + Cpx + Grt + Pl + IIm + Bt + Am ±Rt), to a synkinematic mostly “wet” eclogitic mineral assemblage is preserved. The latter consists of Grt + Opx + Am + Ab-Czo symplectites + Bt + Opaque phases (e.g. Ilm) ±phengite, as well as omphacite + garnet (Figure 3.1 B, C), where the reaction advanced further or local chemical domains supported this assemblage (Austrheim, 1987; Lund and Austrheim, 2003; John et al., 2009; Putnis and Austrheim, 2010; Müller, 2013). The replacement of magmatic plagioclase by Ab-Czo symplectites (e.g., Wayte et al., 1989), along with the widespread formation of amphiboles and of Grt-Omp assemblages, occurs where transport during reactions has been enhanced (e.g., Mørk, 1985; John and Schenk, 2003; Putnis and Austrheim, 2010). All these developments positively correlate with the observed strain gradient, and show that eclogitization of the gabbro was driven by the close interplay of infiltration of externally derived fluids and deformation (Mørk, 1985; Austrheim, 1987; Krabbendam et al., 2000; Lund and Austrheim, 2003; Labrousse et al., 2010; Putnis and Austrheim, 2010).
3.2 Geological Setting

Figure 3.1: A) Optical microscope image illustrating the mineral phases and microstructures present in the metagabbros. B) Intermediate strain domain: old olivine cores are now replaced by orthopyroxene-amphibole symplectites (Opx-Amp Symp). Relict cores of magmatic clinoxyroxene are present, and they are surrounded by a thin rim of omphacite, which is also present between garnet and orthopyroxene-amphibole symplectites (Opx-Amp Symp). C) More deformed sample: symplectites of albite-clinozoisite (Ab-Czo Symp) are replacing the plagioclase; omphacite surround relict clinoxyroxene and orthopyroxene-amphibole symplectites.
3.3 Methods

The methods used to analysed Kråkeneset metagabbros are described in chapter 2, section 2.4. Computed x-ray microtomography has been combined with SEM, EDS, EMPA and EBSD analyses in order to provide a multi-dimensional characterization of the process which led to the compositional transformation from "dry" gabbros to hydrous eclogites within the shear zone.

While $\mu$CT quantifies the spatial distribution of the mineral phases and their volumes, shapes and connectivity with increasing deformation, chemical and EBSD analyses offer information on the active deformation mechanisms that transformed the pristine olivine metagabbros into deformed omphacite-garnet eclogites.
3.4 Results

3.4.1 Petrographic characterization

In the low strain domain, at larger distance to the shear zone centre (sample 066B2), although the magmatic gabbroic assemblage is still preserved, all mineral phases show reaction textures (Figure 3.2 A-B). These reactions, related to sluggish kinetics, were triggered by fluid-rock interactions: the amount of the reacted rock volume decreases with the distance to the hydrous shear zone (Lund and Austrheim, 2003; John et al., 2009). Olivine cores (Fo$_{54}$Fa$_{45}$Tep$_{0.3}$) are surrounded by innermost coronas of fibrous orthopyroxene followed by a $\sim 50$ µm wide poikiloblastic corona of garnet (Alm$_{63.3}$Grs$_{19.8}$Py$_{14.9}$, Figure 3.2 A) and fibrous amphibole (hornblende) at the contact with plagioclase. The grain size of olivine cores is variable, generally of the order of a few hundred micrometers. Olivine grains exhibit cleavage planes in different orientations. While orthopyroxene coronas seem to have a constant width around olivine grains, garnet coronas vary in thickness. These microfabrics are similar to the ones previously described by Mørk (1985), Krabbendam et al. (2000), Lund and Austrheim (2003), and Müller (2013). According to Mørk (1985), the coronas between olivine and plagioclase form through reaction: Ol + Pl (An) + Cpx + H$_2$O $\Rightarrow$ Opx + Grt + Am + Pl (Ab). It is unclear whether these coronas formed as products of synkinematic fluid infiltration (Krabbendam et al., 2000; Lund and Austrheim, 2003) or as results of late-magmatic processes (Mørk, 1986). However, I speculate that amphibole is indicative of the external influx of hydrous fluids upon shear zone formation, as shown later by CPO of hornblende in the high strain zone (Austrheim, 1987; Austrheim et al., 1997; Engvik et al., 2000; Labrousse et al., 2004; Putnis and Austrheim, 2010). Truly eclogite-facies assemblages are only observed at fluid pathways terminations or where fluid availability and/or deformation enhanced the size of the reacted domains allowing for sufficient material transport and thus bulk equilibration resulting in the formation of an omphacite-garnet assemblage (Figure 3.1) (Lund and Austrheim, 2003; John et al., 2009; Putnis and Austrheim, 2010). However, the overall dominance of amphibole over omphacite in the samples indicates that the chemical equilibrium of the system was local, and in favour of garnet-amphibole assemblage, instead of garnet and omphacite. In those cases where plagioclase reacted in rather isochemical systems, the high-pressure assemblage is dominated by the Ab-Czo symplectites $\pm$ amphibole $\pm$ garnet (Lund and Austrheim, 2003; John et al., 2009).
In the intermediate strain domain (sample 061751), the texture changes (Figure 3.2 C, D). Olivine grains are pseudomorphically replaced by orthopyroxene and orthoamphibole intergrowth, which is surrounded by a thin (a few µm wide) rim of omphacite (Figure 3.1 B, see also Lund and Austrheim, 2003). Mørk (1985) interprets the discontinuous growth of thin omphacite layers between orthopyroxene and garnet coronas to have formed through: \((\text{Ol}) + \text{Grt} + \text{Opx} + \text{Am} + \text{Pl} \Rightarrow \text{Omp} + \text{Spin}\). However, the fact that, in contrast to Mørk (1985), spinel inclusions were not observed, points to this reaction being incomplete in the samples, and mineral growth limited by material supply (see also Mørk, 1985; John et al., 2009). Clinopyroxene grains in this domain appear less regular and altered by cloudy patches of Fe-Ti oxides as a result of destabilization through the reaction: \(\text{Cpx (Aug)} + \text{Na} \Rightarrow \text{Na-Aug} + \text{Fe-Ti oxides}\), in which Na-Aug constitutes a second generation of more altered clinopyroxene with increase Jd-component but reduced Ti and Fe contents (Cpx₂) (Mørk, 1985). Garnet and amphibole are still present, but they do not form clear corona structures anymore (Figure 3.2 B). The 3-dimensional distribution of garnets still resemble coronas where decaying olivine grains are more completely replaced by orthopyroxene, but generally garnet grains develop euhedral crystals and form disconnected and more elongated aggregates (Figure 3.5 B). Towards the shear zone, all plagioclase is replaced by clinzoisite and albite symplectites through the reaction (Figure 3.1 B, C): \(\text{Pl (An)} + \text{H}_2\text{O} \Rightarrow \text{Czo + Ab symplectites}\) (Wayte et al., 1989; Lund and Austrheim, 2003; John et al., 2009; Müller, 2013) (Figure 3.1). The Czo+Ab symplectites are preserved without evidence of any later overprint, and are considered to have formed as prograde replacement of plagioclase in a fluid-mediated system, indicating a metastable prograde reaction (Wayte et al., 1989). Therefore, in the presence of amphibole, omphacite associated with these delicate symplectite textures indicates a prograde conversion of the gabbro to an eclogite in which fluid infiltration was synkinematic and linked to the progress of reaction and deformation (Figure 3.1 B).

In the most deformed sample (0618), all mineral phases are aligned parallel to a mylonitic foliation. The foliation is defined by a compositional layering of elongated orthopyroxene-amphibole symplectites and garnet, forming isolated elongated clusters >100 µm wide and several hundred µm long (Figure 3.2 E-F). Some of garnet grains still exhibit faceted crystals (Figure 3.5 C). Omphacite is present at the margins of relict magmatic clinopyroxene grains and of orthopyroxene-amphibole symplectites (Figure 3.1 C).
3.4 Results

Figure 3.2: BSE images of Krakeneset samples and corresponding microtomographic datasets, from low to high strain domain respectively: A) Sample 066B2 (Low strain)- Olivine grains surrounded by complex coronas of orthopyroxene, garnet and amphibole. B) 3-dimensional dataset of low strain domain: high-pressure amphibole-garnet coronas surround olivine grains (dimensions 1503 x 1196 x 1831 cubic voxels). Note the variable thickness of amphibole. C) Sample 0617 (Intermediate Strain)- In the intermediate strain domain, olivine cores are replaced by orthopyroxene, while garnet and amphibole are not part of the corona structures any more. D) Corresponding microtomographic dataset (dimensions 1322 x 1219 x 2023 cubic voxels). E) Sample 0618 (High Strain)- The high strain domain is characterized by a compositional layering of ribboned garnet and plagioclase versus orthopyroxene and amphibole rich layers. F) Microtomographic dataset relative to the high strain domain (dimensions 1313 x 1234 x 1980 cubic voxels): note garnet grains behaving as rigid objects in a more ductile matrix of orthopyroxene and amphibole.
3.4.2 Chemical compositions and mineral chemistry

Garnet compositions in the three samples were measured using electron microprobe analyses, in order to confirm the chemical evolution of garnet with respect to the deformation history (Figure 3.3, Figure 3.4). With increasing deformation, garnet compositions become more Alm-rich (Figure 3.3), an expected trend for a gabbro that is gradually equilibrating under eclogite-facies P-T conditions. Within the low-strain domain, high CaO concentrations (XGrs) are represented by garnet in the proximity of Ca-rich phases (e.g. plagioclase). In the high strain domain the compositional maps show that some garnet displays CaO zoning (5-12 wt. %) and zoning pattern similar to those observed in low strain domain (Figure 3.4). It seems that locally these garnets represent collapsed former coronas (a’, b’ in Figure 3.4 C). Furthermore, fine-grained garnets (Figure 3.4 C to the left) represent highly fragmented and collapsed former coronas.

![Garnet compositions plot](image)

**Figure 3.3:** Grs-Alm-Py plot showing garnet compositions from EMPA analyses, as single measurements across different grains. End-members values, calculated as average from the single measurements, are presented in the graph by the large symbols. Filled symbols represent compositions closer to the plagioclase source. Empty symbols represent compositions closer to Fe-Mg-rich phases. With increasing deformation, garnet compositions become more Alm-rich, a trend expected for a gabbro that is equilibrating under P-T-t conditions of eclogite facies. In Appendix B, Figure B.9, representative structural formulae are reported for the three samples.
3.4 Results

Figure 3.4: Compositional maps for CaO and MgO for the low (A-C) and high (B-D) strain domains, obtained using XMapTools v. 2.3.1 (Lanari et al., 2014). CaO and MgO do have the same compositional zoning in the most deformed sample. Nevertheless, some grains do have a higher content in CaO and MgO, reflecting an equilibrium towards Alm-rich compositions. Further left in Figure C, garnets are fragmented and forming a fine-grained matrix, indicating collapse of an old pre-existing corona. Many garnets in the high strain domain have low CaO, reflecting an equilibrium towards Alm-rich compositions. Nevertheless, some grains do have a higher content in CaO and MgO (A-C and high (B-D) strain domains), obtained using XMapTools v. 2.3.1.
Chapter 3. The morphological evolution of garnet grains

3.4.3 4D spatial evolution of garnet grains

A subvolume with dimensions of $600^3$ voxels ($\sim 0.5 \text{ mm}^3$) was extracted from each of the three microtomographic datasets, through image analysis procedure, to visualize the 3-dimensional distribution of garnet (Figure 3.5). In the subsequent label analysis, garnet distribution was evaluated and quantified in the original, statistically representative $7 \text{ mm}^3$ subvolumes (Figure 3.2 B, D, F and Figure 3.7). In the label analysis, all garnet clusters that consist of face-connected voxels and are larger than $125 \text{ cubic voxels}$ were considered ($\sim 275 \text{ \mu m}^3$). This allowed to relate the following observations to the 3-dimensional petrography presented above. The volumetric quantification of the segmented garnet data shows that the garnet volume increases into the shear zone, from $6\% (\pm 2.5\%)$ in the low-strain sample, to $11\% (\pm 3\%)$ in the intermediate strain sample, and $20\% (\pm 4\%)$ in the high-strain sample.

Figure 3.5: The figures illustrate the results of segmentation on garnet grains. Top: cropped volumes of original datasets ($\sim 0.5 \text{ mm}^3$); Bottom: garnets rendered in purple. Fog is added within the datasets to better render the 3D architecture. A) Low strain, B) Intermediate strain, C) High strain. Note 3D orientation and texture of garnet grains. Note the presence of more faceted grains in the intermediate and high strain domain.

The visualisation confirms that in the low strain domain, garnet forms voluminous interconnected coronas around orthopyroxene and decaying olivine grains (Figure 3.5 A). It also becomes apparent that different olivine cores have garnet rims with different thicknesses. Measurements of garnet corona thicknesses around five different olivine
grains show an average thickness of 60 µm with standard deviations that vary from 10 to 35 µm in the most complex coronas. Where two olivine grains neighbour each other, garnet coronas become almost twice as thick. There seems to be no correlation between the thickness of the garnet- and the amphibole rims, which should have evolved in unison (Mørk, 1985, 1986; Johnson and Carlson, 1990). Despite their considerable spatial extent, garnet coronas do not enclose olivine grains entirely, which leaves dormant reactants in direct contact with each other (cfr. Appendix B, Figure B.6). The resulting baseball-glove shaped domains also do not show any preferential spatial orientation with respect to the kinematic framework of the shear zone (cfr. Appendix B, Figure B.6). The total garnet volume in the analysed subvolume is accommodated by 1116 garnet voxel clusters (cfr. Appendix B, Table B.2). The label analysis shows that the garnet population is dominated by one large interconnected garnet voxel cluster that percolates across the entire subvolume (Figure 3.7 A). This cluster accounts for 83 % of the entire garnet volume in the sample (Figure 3.6 A, B). Garnet voxel clusters between $2.2 \times 10^6$ and $3.08 \times 10^7 \ \mu m^3$ account for 11 %, whereas voxel clusters $< 2.2 \times 10^6 \ \mu m^3$ do not contribute substantially to the total garnet volume (Figure 3.6 B). Segmented data were submitted to a numerical volume erosion process to learn more about the spatial arrangement of garnet (see supplementary data in Appendix B and Table B.3). Garnet interconnectivity persists through the volume erosion, which evidences how tightly individual garnets grains are linked in the coronas (see Appendix B). In the eroded data, the garnet volume forms 2796 voxel clusters (see Appendix B, Table B.3). The largest interconnected voxel cluster dramatically decreases in volume from $4 \times 10^8 \ \mu m^3$ to $10^8 \ \mu m^3$, now accounting for only 35 % of the total volume. The eight largest interconnected voxel clusters ($> 2.2 \times 10^6 \ \mu m^3$) account for 89 % of the total garnet volume as seen in the cumulative frequency diagram (Figure 3.6 B). The erosion process also leads to a substantial increase in frequency for sizes smaller than $10^4$ cubic $\mu m^3$ (Figure 3.6 A), which is in contrast to the intermediate and high-strain datasets. This is interpreted as to be related to the presence of many non-spherical objects, which are divided in smaller objects during the erosion process (Figure 3.8 B).

The visualisation of garnet in the intermediate strain domain shows that the larger garnet voxel clusters form complexly-shaped rims around orthopyroxene aggregates that likely have their origin in former coronas (Figure 3.7 B). In this sample, the garnet volume is made up of 12068 garnet voxel clusters. This almost ten-fold increase over the low strain sample is essentially being accommodated by the smallest ($< 10^5 \ \mu m^3$) and largest ($> 6 \times 10^8 \ \mu m^3$) voxel cluster size fractions (cfr. Appendix B, Table B.2). A similar number of voxel clusters in the size region of $10^5 \ \mu m^3$ was detected, whilst a particularly large number of voxel clusters with volumes between $10^3$ and $10^4 \ \mu m^3$
were found. Again, the largest 10 voxel clusters (> $2.2 \times 10^6 \, \mu m^3$) account for over 90% of the total garnet volume. The largest interconnected voxel cluster, which is larger than in the low-strain sample ($4 \times 10^8 \, \mu m^3$ to $6.5 \times 10^8 \, \mu m^3$) develops through the subvolume and accounts for 80% of the total garnet volume. The garnet voxel clusters in the range of $2.6 \times 10^5$ to $4 \times 10^6 \, \mu m^3$ are often formed by isolated, euhedral and potentially newly formed garnet grains (Figure 3.5, Figure 3.7 B; see section 3.5). Voxel clusters smaller than $10^5 \, \mu m^3$ are arranged in patchy clouds surrounding bigger interconnected voxel clusters. In the numerically eroded data, the number of garnet voxel cluster reduces to 4995. Since a numerical erosion cannot lead to voxel cluster coalescence, this decrease reflects a sensitivity to the disappearance of volumetrically small voxel clusters in the procedure (Figure 3.6 C, Table B.3, Figure 3.8). In the erosion process, the largest voxel cluster breaks apart to form two smaller voxel clusters, which together account for 70% of total garnet volume (Figure 3.6 D, cfr. Appendix B, Figure B.7).

The visualization of the microtomographic data shows that in the most deformed sample, the garnet voxel clusters define a mylonitic foliation. In this subvolume, garnets contribute to a deformation microfabric; the garnet voxel clusters define the compositional layering observed in the SEM analysis (Figure 3.7 C). Additional analyses, conducted using the software package Quant3D (Ketcham and Ryan, 2004), revealed that most of the garnet voxel clusters in this sample have an oblate shape (cfr. Appendix B, Figure B.8). Garnet in the subvolume is organized in 9297 voxel clusters (cfr. Appendix B, Table B.2). A total of 46 voxel clusters have a volume larger than $2.2 \times 10^6 \, \mu m^3$, and they account for 86% of the total garnet volume (Figure 3.6 F). The absolute frequency-size distribution is self-similar, with no major local variations between the size classes. This trend is confirmed by the cumulative plot (Figure 3.6 F), which shows that all size classes contribute progressively towards the total garnet volume, and is in contrast to the other two samples. Numerical erosion reduces the number of garnet voxel clusters to 8014, of which 62 are larger than $2.2 \times 10^6 \, \mu m^3$ and accommodate 81% of garnet total volume (cfr. Appendix B, Table B.3). The reduction in total voxel cluster number is accommodated by all size fractions, which indicates that the voxel clusters have shapes that withstand a numerical erosion process (Figure 3.6 E, F).

### 3.4.4 EBSD analysis: Misorientation of garnet grains in the shear zone

Garnet in the three samples was analysed using EBSD to investigate the dominant deformation mechanisms that contributed towards the evolution of the microfabric
3.4 Results

Figure 3.6: Garnet voxel cluster size distribution for non-eroded (solid lines) and eroded (dashed lines) data. From low to high strain, there is an increase in frequency for all size classes with increasing strain. Note the presence of the very large interconnected garnet voxel cluster in the low strain domain (blue solid curve), while the presence of much smaller sizes in the most deformed sample. The sketch on the top left corner illustrates the erosion process and the effects of particle size and shape: some particles might completely disappear. A, B) Absolute frequency and cumulative volume, respectively, for the low strain sample. C, D) Absolute frequency and cumulative volume, respectively, for the intermediate strain sample. E, F) Absolute frequency and cumulative volume, respectively, for the high strain sample.

in garnets. Garnet and orthopyroxene in the low strain sample exhibit frequent low angle boundaries (misorientation between 3° and 10°). The phase map of a coronitic domain around magmatic olivine shows that orthopyroxene and hornblende grows
Chapter 3. The morphological evolution of garnet grains

Figure 3.7: Label analysis of the studied samples. A) 3D volume rendering of labels relative to low strain domain (dimensions 1503 x 1196 x 1831 cubic voxels). B) Intermediate Strain (dimensions 1322 x 1219 x 2023 cubic voxels). C) High strain (dimensions 1313 x 1234 x 1980 cubic voxels). Individual disconnected aggregates of garnet are identified with different colours.

Figure 3.8: Effects of erosion-dilation on morphology (A) and on the degree of interconnectivity (B). A) Spherical objects retain their morphologies after multiple erosions. However, for non-spherical objects, the erosion process has a marked effect. This is particularly enhanced on the degree of connectivity, which is reduced since the erosion process breaks interconnectivity points (B).

as fibrous crystals: the long axis of orthopyroxene and hornblende are perpendicular to the reaction interface (cfr. Appendix B, Figure B.1 A). In the case of hornblende, the elongation is parallel to the <001> axis (cfr. Appendix B, Figure B.2 F). The inverse pole figure map (IPF) of garnet, shown with respect to the E-W direction (i.e. approximately equivalent to the normal to the reaction interface and parallel to the elongation direction of hornblende) (Figure 3.9 A), highlights the presence of low-angle boundaries, which correspond, in the local misorientation map (cfr. Appendix B, Figure B.1 C), to internal misorientation zones with up to 9° of misorientation in garnet. A misorientation profile across them does not show any progressive distortion of the crystal lattice, but rather a sudden jump in misorientation (Figure 3.9 B). The average local internal misorientation of grains is very low, on the order of 1°, i.e. within the error of measurement. The misorientation axes for misorientation angles of 3-10° do not show clear maxima in crystal coordinates (Figure 3.9 C). Pole figures show that coronitic garnet grains are not elongated parallel to specific crystallographic directions.
In the intermediate strain sample, the spatial density of low angle boundaries is highly variable. A local misorientation map shows that the interiors of garnet grains are virtually undeformed (average local misorientation on the order of 1°), and that there are bands with high misorientation up to 9° (Figure 3.9 D). A misorientation profile across one of the bands shows a rather abrupt misorientation jump (of up to 8°) (Figure 3.9 E). Similar to the low strain domain, the misorientation axes for misorientation angles of 3-10° do not show clear maxima in crystal coordinates (Figure 3.9 F). The IPF map and the associated pole figures show a weak preferred orientation of garnet, with voxel clusters of grains preferentially oriented with their <111> parallel to the stretching lineation of the shear zone (cfr. Appendix B, Figure B.3 A, Figure B.3 E). The IPF map shows that garnet grains range in size between 10-20 μm and 200 μm.

In the high strain sample, the density of low angle boundaries in garnet is very low, and they are typically present only in grains larger than 50 μm (Figure 3.9 G). The phase map indicates that individual garnet grains range in size from ca. 10 μm to ca. 150-200 μm and are dispersed in a matrix of hornblende, orthopyroxene and minor biotite (cfr. Appendix B, Figure B.4 A). Garnet grains are internally strain-free (average local misorientation is < 1°), and again, there is no progressive accumulation of misorientation towards the few internal high misorientation bands (as indicated by the local misorientation map in Appendix B, Figure B.4 B). Less frequently, a progressive accumulation of lattice distortion (of up to 4°) towards the low angle boundaries was observed (Figure 3.9 H). The misorientation axes for misorientation angles of 3-10° do not show clear maxima in crystal coordinates (Figure 3.9 I). Pole figures of garnet show only weak maxima of <100>, one of which is oriented subparallel to the stretching lineation (cfr. Appendix B, Figure B.4 C, Figure B.5 A, Figure B.5 B). Neighbouring grains are typically characterized by large misorientations (> 30°, cfr. Appendix B, Figure B.4 F). In contrast, hornblende shows a crystal preferred orientation (CPO) with the c-axis oriented subparallel to the stretching lineation. This CPO of hornblende has been commonly observed in lower crustal shear zones where hornblende grew synkinematically to deformation (Berger and Stünitz, 1996; Getsinger and Hirth, 2014; Menegon et al., 2015). Combined, the crystallographic data point to a negligible contribution of crystal plasticity to garnet deformation.
Figure 3.9: EBSD analysis results for garnet. Low strain: A) IPF map superposed on a pattern quality (Band Contrast) map. B) Profile X-Y, location in figure A). C) Misorientation axis by crystal coordinates for low angle boundaries (3-10°). Intermediate strain domain: D) IPF map. E) Profile X-Y, location in figure D; F) Misorientation axis by crystal coordinates for low angle boundaries (3-10°). High strain: G) IPF map. H) Profile X-Y, location in figure G; I) Misorientation axis by crystal coordinates for low angle boundaries (3-10°).
3.5 Discussion

3.5.1 Strain-dependent evolution of garnet microfabrics in the Kråkeneset shear zone

The observations reported above offer a detailed picture of the synkinematic evolution of garnet in this deep-crustal shear zone. The µCT data indicate that, across the studied shear zone margin, from low to high strain, garnets evolve from a highly interconnected coronitic texture to a tectonic microfabric, where they are organized in oblate aggregates and define the foliation of the shear zone (Figure 3.7 C). Simultaneously, the garnet volume in the rocks more than triples. Based on chemical analyses, which revealed a partial local equilibration of garnets grains at eclogite facies (Fe-rich), the oblate sheared aggregates are interpreted as having formed by the progressive, synkinematic disintegration and rearrangement of coronas in combination with the simultaneous nucleation and coalescence of garnets grains at similar P, T, X metamorphic conditions (Figure 3.10).

Garnet coronas originally formed as the high-pressure reaction products of a prograde metastable reaction between olivine and plagioclase by the coalescence of nuclei. As strain localises in the shear zone, these garnet coronas are broken apart and start to disintegrate (Figure 3.10-1, 2). At this stage, the garnet voxel clusters do not reflect a deformation microfabric yet, and the largest garnet cluster is still interconnected through the entire sample forming complexly-shaped rims around orthopyroxene porphyroclasts that have replaced olivine. New garnet grains nucleate in between these large voxel clusters but are still small at this stage, while existing garnet grains are overgrown and increase in volume. At the highest level of strain, the former garnet coronas have been deformed and re-arranged by granular flow in a ductively deforming matrix, leading to a mylonitic deformation microfabrics defined by oblate garnet voxel clusters (Figure 3.2, Figure 3.7 C and Figure 3.10-3).

3.5.1.1 Where does all the garnet go?

The results of the label analysis, and in particular the evolution of different size classes of garnet voxel clusters, reveal how the volumetric increase in garnet is accommodated and what processes affect the garnet population across the shear zone margin. The overall increase in the number of garnet voxel clusters into the shear zone reflects the synkinematic formation of a well-dispersed garnet population (Figure 3.6). This is achieved by the coeval activity of three processes, the fragmentation and
breakup of garnet coronas, the formation of overgrowth rims, and the nucleation of new garnet crystals (Figure 3.10):

1. The increase in the number of garnet voxel clusters, particularly the large ones, with increasing strain clearly reflects a reduction of garnet interconnectivity. The largest voxel cluster in the low and intermediate strain domain accounts for 80% of the overall garnet volume, whereas a similar volume proportion is accommodated by 46 voxel clusters (> 2.2 x 10^6 µm^3) in the most deformed sample.

2. The transition from the low strain- to the intermediate strain domain sees a complete reorganisation in the population of the smallest garnet voxel clusters (Figure 3.6 C). Voxel clusters ≤ 4.1 x 10^3 µm^3 increase in number from 698 to 11239 (cfr. Appendix B, Table B.2). These clusters occur dispersed in between the larger clusters, without any obvious textural link. As the total amount of garnet volume increases, they cannot be fragments of initial coronitic garnet; therefore this population of smallest voxel clusters is interpreted to be the product of nucleation and may evidence pervasive fluid infiltration (see following section).

3. In contrast, the increase in the number of intermediate-sized voxel clusters with volumes between 2.6 x 10^5 and 4 x 10^6 µm^3, which is particularly apparent in the intermediate strain domain, is inferred to be related to overgrowth. The

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**Figure 3.10:** Schematic sketch illustrating the evolution of reaction microfabrics, and in particular of garnet grains. 1) Low strain domain. 2) Intermediate strain. 3) High strain. See text for discussion.
3.5 Discussion

3-dimensional visualisation shows that garnet voxel clusters have euhedral or semi-euhedral shapes, which is congruent with this mechanism (Padrón-Navarta et al., 2008).

3.5.1.2 What the morphological operator “Erosion” reveals about the garnet distribution

The frequency diagrams reveal that the number of voxel clusters does increase as a response to erosion in the low strain domain for smaller voxel cluster sizes (< $10^4 \mu m^3$, Figure 3.6 A, B) and in the intermediate strain domain for the largest interconnected cluster (cfr. Appendix B, Figure B.7). This indicates that a substantial number of voxel clusters exhibits cross-sectional diameters short enough to respond to a single erosion step. By acting as predetermined breaking points, these weak bridges become crucial in the disintegration of the garnet coronas as the rock transitions to the intermediate strain microfabrics (Figure 3.10-1). As a consequence of this break-up, a larger proportion of the garnet volume is accommodated by smaller clusters in the eroded dataset (Figure 3.6 B). In the intermediate strain domain, the absolute frequency of voxel clusters < 5 x $10^4 \mu m^3$ decreases significantly as a consequence of morphological erosion (Figure 3.6 C, cfr. Appendix B, Table B.2 and Table B.3). These are the voxel clusters that make up the patchy clouds in between the larger garnet aggregates. Many of these small clusters are apparently susceptible to annihilation in a single erosion step, which points towards a significant deviation from sphericity in this voxel cluster population.

In the high strain domain, the garnet voxel clusters retain their self-similar frequency-size distribution through the morphological erosion process in the high strain domain (Figure 3.6 E, F). However, the changes to the frequency of voxel clusters in the different bins seem to reflect a slight decrease in the fractal dimension (Figure 3.6 E, F). A new population of voxel clusters with volumes <10^3 $\mu m^3$ is generated from larger clusters, and the largest voxel cluster halves in size (from 1.1 to 2.2 x $10^8 \mu m^3$).

3.5.1.3 Micromechanisms involved

The EBSD data indicate that the mechanism by which the garnet coronas are disintegrated does not involve crystal plasticity by means of dislocation activity. Whilst garnet was shown to deform by dislocation creep at upper amphibolite to granulite facies metamorphic conditions (Ji and Martignole, 1994, 1996), this was not the case in the sampled shear zone. Misorientation maps and profiles indicate that neighbouring garnet domains show only limited and relative rotations (Figure 3.9). These motions are accommodated by narrow, distinct bands that correspond to low-angle boundaries; the grains themselves show very little internal deformation. The
bands coincide with sudden jumps in misorientations, testifying that they are not subgrains or dislocation walls (Figure 3.9 B, E, H, Viegas et al., 2016). Furthermore, the plots of misorientation axis in crystal coordinates show that the low-angle boundaries are not tied to the host crystallography but rather show a highly dispersed distribution (Figure 3.9 C, F, I). Based on these arguments, the low angle boundaries in the low strain domain are interpreted to be growth features, and probably related to an early stage of coalescence of nuclei. The overall lack of chemical differences amongst the newly formed garnets and their seeds would be congruent with a close initial nucleation spacing of garnets seeds, similar to the observations reported in Whitney and Seaton (2010). On the basis of an almost complete lack of evidence for crystal plasticity, the progressive disintegration and rearrangement of garnet coronas are interpreted as being accommodated by microfracturing and passive granular flow of garnets in a viscously deforming matrix (Trepmann and Stöckhert, 2002). This view is supported by experimental data on garnet rheology (Voegelé et al., 1998; Wang and Ji, 1999; Zhang and Green, 2007), which establish the possibility of brittle garnet behaviour at the inferred metamorphic conditions. Microfracturing and passive granular flow of garnet grains could have been assisted by a fluid phase (Den Brok and Kruhl, 1996; Storey and Prior, 2005; Smit et al., 2011). As it is well established, fluid infiltration played a critical role in triggering eclogitization and strain localisation in dry and ridged precursor rocks (Austrheim, 1987; Austrheim et al., 1997; Engvik et al., 2000; John and Schenk, 2003; Miller et al., 2007; Labrousse et al., 2010; Putnis and John, 2010). The presence of fluids in the system is evident from the hydrous high-pressure mineral assemblage in the shear zone. However, no clear evidence for fluid-assisted deformation mechanisms was found, such as intergranular pressure solution (e. g. Azor et al. (1997) and Smit et al. (2011)), diffusion creep (Den Brok and Kruhl, 1996; Storey and Prior, 2005) or grain-boundary sliding and diffusion creep (Terry and Heidelbach, 2004) to have dominated garnet deformation. However, garnets are interpreted to trace fluid migration pathways to some extent (see following section).

3.5.2 Implications for fluid flow, mass- and element transport

The 3-dimensional spatial arrangement of garnets is not only the result of deformation, but, in the low-strain domain, it also reflects mass transport between plagioclase and olivine grains during their reaction (Austrheim, 1987; Lund and Austrheim, 2003; Labrousse et al., 2010; Putnis and John, 2010). The observations show that garnet coronas are highly interconnected throughout the low strain samples (Figure 3.7 A) and thus, fluid transport must have happened on a trans-granular scale. However, the coronas do not encapsulate and isolate olivine grains from plagioclase, as commonly
thought when observing coronas in two dimensions (Mørk, 1986; Johnson and Carlson, 1990; Keller et al., 2004). Where the coronas did not form, this happened despite the reactants being in direct contact with each other, and obviously the reaction was subdued. Garnet formed where fluids facilitated the reaction and therefore the heterogeneously distributed reaction products are linked to fossilized fluid pathways.

In the intermediate strain domain, syn-reactive fluid-infiltration is testified by the presence of cloudy patches of small garnets, along with the observation that water-bearing minerals are concentrated in the shear zone centre. The abundance of these minerals decreases along the lateral strain gradient away from the shear zone and are absent where the gabbro is undeformed (John et al., 2009). These observations are congruent with those reported in earlier studies by Austrheim (1987), Wayte et al. (1989), Engvik et al. (2001), John and Schenk (2003), and Putnis and John (2010). These studies established that eclogitization in the lower crust can be triggered by an external input of fluids and facilitated by the presence of preferential pathways, such as fractures, which controlled element mobility and defined reaction pathways. However, the data also reveal that there is no systematic arrangement of the garnet coronas with respect to a kinematic framework defined by the deformation microfabrics. It therefore remains unclear what controlled preferential fluid pathways on the grain scale. In an extension to this argument, in the high-strain samples, the oblate garnet aggregates also should have channelized synkinematic fluid flow (see also Austrheim, 1987). The aligned, oblate garnet aggregates, defining the foliation, are interpreted as having acted as fluid barriers and thereby directed synkinematic fluid flow in the shear zone. However, the wettability of different mineral phases have a further effect on preferential fluid pathways, which are therefore controlled by several factors at the micro-scale.
Figure 3.11: Sketch summarising the evolution from an undeformed olivine gabbro towards a deformed omphacite-garnet eclogite, highlighting the role of fluids, mineral reactions and shearing during the evolution.
3.6 Conclusions

4-dimensional quantitative X-ray micro-tomography proved to be an excellent approach to investigate the evolution of metamorphic reaction microfabrics in three dimensions. In combination with established microanalytical methods, it allowed a comprehensive characterization of the processes affecting the evolution of garnet during eclogitization in a shear zone in the Western Gneiss Region, Norway. In particular, it enabled to:

- Capture and monitor the spatial distribution of mineral phases in four dimensions: the X-ray absorption contrast between individual mineral phases in the microtomographic data is sufficient to allow the same petrographic observations than in light- and electron microscopy, but extended to the 3\textsuperscript{rd} and, where strain is considered a proxy for time, 4\textsuperscript{th} dimension.

- Quantify the change in garnet volume across the strain gradient: with increasing deformation, the garnet volume increases from about 6 \% to 20 \%.

- Determine the interconnectivity of garnet grains as a function of strain, with implication for mass transport, syn-reactive fluid flow and rock strength.

- Identify the 3-dimensional geometry of garnet coronas, find that they do not encapsulate olivine grains and have no apparent preferred alignment. Garnet coronas outline fossilized fluid pathways.

- Identify the mechanisms by which garnet is reorganized during shearing: microfracturing, nucleation and overgrowth. These observations point to a mechanical disintegration of garnet coronas during strain localisation and their rearrangement into individual sheared isolated voxel clusters, with the ongoing nucleation of new garnets and overgrowth while the rock was deforming. There is no evidence for crystal plastic deformation, all garnets are internally strain free and in the more deformed samples they show a very weak crystal preferred orientation.

This study clearly shows what 3- or 4-dimensional datasets from reaction microfabrics can add to the understanding of metamorphic processes. A 2-dimensional analysis of deformation microfabrics can lead to incorrect petrological and structural interpretations, and it does omit information that only become available when rocks are investigated in three dimensions.
4D evolution of porosity during ongoing pressure-solution processes in NaCl

“To see a World in a Grain of Sand
And a Heaven in a Wild Flower
Hold Infinity in the palm of your hand
And Eternity in an hour”.
—Auguries of Innocence, William Blake

ABSTRACT
This chapter describes a suite of experiments performed to investigate the evolution of porosity during deformation-driven pressure-solution processes, using NaCl as rock-analogue material. The processes were analysed using μCT, and monitor the evolution over time, yielding a 4D microtomographic dataset. The influence of uniaxial load, and bulk sample composition modified by the presence of phyllosilicates and/or glass beads was investigated. Greater uniaxial loads, and the presence of phyllosilicates within the deforming NaCl columns was found to enhance pressure-solution processes.

Under these conditions, pressure-solution triggers a significant reduction in pore space, and a considerable degree of grain indentations. The pore space becomes highly disconnected in the presence of phyllosilicates, with important implications for fluid flow, as shown from the skeletonization analyses. Furthermore, the phyllosilicates localise the process, as shown by the pore size and strains distributions. In the case of glass beads, the pore space and pore interconnectivity decrease, but less efficiently than in the presence of phyllosilicates. SEM images show high degrees of indentations at NaCl-NaCl interfaces and at the boundary with glass beads. The combination of μCT with 3D-DIC and SEM imaging proves to be an efficient analytical method for
Author Contributions: The idea of performing pressure-solution using NaCl as rock-analogue came after discussion between my supervisor Dr. Florian Fusseis and Prof. Chris Spiers at the Gordon Research Conference in 2014. The cell and loading system was designed by my supervisor Dr. Ian Butler and machined in our mechanical workshop at the School of Geosciences. Further experiments followed, some of which have been described in a publication which considers the spatio-temporal evolution of porosity in the presence of phyllosilicates, and will be submitted to the journal EPSL. Other experiments, which test the effects of glass beads on the process, will be described in other future publications. Volumetric Digital Image Correlation (3D-DIC) analyses on the microtomographic data have been possible thanks to the Tomowarp2 code developed by Stephen Hall and Erika Tudisco (Lund University) in collaboration with Edward Andó (University of Grenoble and Laboratoire 3SR-CNRS). Data processing for 3D-DIC was performed on the Terracorrelator data cluster in Edinburgh.
Chapter 4. Pressure-solution processes

4.1 Introduction

Pressure-solution creep (PSC) is a common deformation mechanism in the upper crust. It represents a solution mass transfer process that involves dissolution at "grain notches, diffusive mass transfer along grain boundaries and re-precipitation of dissolved material in unstressed areas" (Rutter, 1983). The chemical and physical alterations resulting from the pressure-solution process critically affect both the porosity and hydraulic properties of the rock, which directly influence fluid flow and element mobility. Pressure-solution processes are present under low-grade metamorphic and late diagenetic conditions (Park and Schot, 1968; Rutter, 1983). Due to their occurrence in many lithologies, pressure-solution processes are an excellent case study for fluid-rock interaction and strain localisation. Despite the numerous lab experiments that have been conducted, many aspects of the spatio-temporal evolution of porosity and permeability during pressure-solution creep remain poorly understood (Fletcher and Pollard, 1981; Carrio-Schaffhauser et al., 1990).

While the rates of pressure-solution creep in silicates and carbonates are slow and make these materials impractical for anything other than very long-term laboratory investigations, compaction experiments have demonstrated that NaCl samples deform sufficiently fast to study pressure solution creep processes in a lab environment at room temperature (Spiers et al., 1990; Gratier, 1993; Bos et al., 2000b).

Understanding the effect of pressure-solution creep on the mechanical and hydraulic properties of rocks has important implications in reconstructing crustal strength profiles. As reported by Bos et al. (2000b), the rheological behaviour of major fault zones might deviate from Byerlee’s law under diagenetic and hydrothermal conditions. This deviation is related to a sensible weakness of intra-plate fault zones due to increasing pore fluid pressures that lower the principal stresses and consequently reduce fault strength. On the other hand, Hickman and Evans (1995) proposed that pressure-solution can cause fault healing by increasing the contact area and degree of gouge compaction. Furthermore, the spatio-temporal evolution of porosity during PSC has important implications for carbonate and petroleum reservoirs geology (Ehrenberg and Nadeau, 2005; Ehrenberg, 2006), as it can substantially modify fluid pathways and change permeabilities. These aspects have been investigated over a number of different lithologies in relation to mechanical and chemical processes: sandstones (Heald, 1955; Sprunt and Nur, 1976; Boer et al., 1977; Sprunt and Nur, 1977; Bjørkum et al., 1998; Ehrenberg and Nadeau, 2005), carbonates (Renard, 2004; Ehrenberg and Nadeau, 2005; Ehrenberg, 2006) and quartzites (Gratz, 1991).
Despite numerous laboratory experiments, the mechanisms governing the pressure-solution process remain poorly understood. The dynamic behaviour of porosity evolution during PSC has not been characterized. In recent decades, many studies have focused on a 2D characterization of the process, but it is evident that pressure-solution depends on many factors and its creep laws critically depend on an exact knowledge of these factors, which cannot be fully derived from 2D analyses alone. Despite the work of Renard et al. (2004) and Heap et al. (2014), the pressure-solution process still lacks a multi-dimensional characterization. Furthermore, stylolites have been intensively studied, but the theoretical models for the origin and propagation of stylolites lack experimental data verification (Fletcher and Pollard, 1981; Carrio-Schaffhauser et al., 1990). There is no experimental study of the evolution of fluid-rock interaction and dynamic porosity architecture around propagating stylolite tips, and hence it is unclear which and how dynamic transport properties are affected by the formation of stylolites. Stylolite propagation has never been reproduced on the time-scale of laboratory experiments, leaving the spatio-temporal evolution of porosity during ongoing pressure-solution processes uncharacterized.

Moreover, the 4D analysis of the microstructural evolution of NaCl grains and pore space enables a better understanding of the role of PSC on the rheological properties of rock-salt, with implications for salt-based repository systems (nuclear radioactive waste) and salt mining (Urai et al., 1986; Spiers et al., 1990; Urai and Spiers, 2007; Urai et al., 2008). Successful management of safe radioactive storage sites on salt deposits critically depends on an accurate knowledge of the hydro-mechanical properties of rock-salt.

The combination of 4D quantitative X-ray microtomography with 3D-DIC (Digital Image Correlation) will allow mapping of the evolution of the pressure-solution process during ongoing compaction, and it will provide a multi-dimensional characterization of the process and porosity evolution. 3D-DIC has been previously applied in combination to X-ray microtomography studies (Lenoir et al., 2007; Hall et al., 2010; Charalampidou et al., 2011; Desrues and Andò, 2015; Torabi et al., 2015), but this is the first time it has been applied to determine the internal deformation of the samples and absolute strain rate evolution during pressure-solution processes.
4.2 Theoretical background

Pressure-solution processes have been investigated for decades and yet despite the knowledge that they constitute a common fluid-rock interaction mechanism, the creep laws that control the process remain poorly understood (Gratier et al., 2013). In fact, many factors contribute to the thermodynamics and kinetics of the process. Some factors may increase the rate of the process by many orders of magnitude, such as the nature of the grain-boundary interface (Gratz, 1991; Den Brok, 1998; Dysthe et al., 2002; Gratier et al., 2013).

Gratier et al. (2013) summarized the parameters governing pressure solution creep:

1. The difference in chemical potential and in stress concentrations between the dissolution and deposition zone, which causes the mass transfer through a fluid phase, constitutes the driving force of the mechanism (Paterson, 1995).

2. The rates of dissolution, transfer and deposition control the kinetics of the entire process. The reaction kinetics of the PSC process are described by the rate-limiting step, which is the slowest step of a reaction. In NaCl, reaction kinetics are known to be transport (diffusion)-controlled (Spiers and Brzesowsky, 1993).

3. The length scale of the process is controlled by the diffusion through a fluid phase. Several models have been proposed for the interface stability (see section 4.2.1.1).

Many studies have been conducted in order to better understand the laws governing PSC and its thermodynamic and kinetic behaviour.

4.2.1 Thermodynamics and kinetics of PSC

The relationship between the driving force of PSC (difference in chemical potential) and the diffusive mass flux, $J$, of a component $x$, along a flat interface between two homogeneous spherical grains is described by the Fick’s law (Rutter, 1983; Lehner and Bataille, 1985; Lehner, 1995; Lehner and Leroy, 2004):

$$ J_x = -L_\alpha \frac{d\mu_\alpha}{dx} $$

where $L_\alpha$ constitutes the phenomenological mobility coefficient, and $\frac{d\mu_\alpha}{dx}$ represents the gradient in chemical potential. From this equation, a constitutive flow
4.2 Theoretical background

law for the strain rate, $\dot{e}$, can be calculated (Rutter, 1983):

$$
\dot{e} = A L_\alpha \sigma V_\alpha w / d^3
$$

(4.1)
in which $A$ is a dimensionless constant, $\sigma$ represents the applied uniaxial stress, $w$ is the effective thickness of the intergranular diffusion window and $d$ is the grain diameter. $V_\alpha$ represents the volume of the solid over a stressed surface. It is clear from this equation that the strain rate is inversely proportional to the cube of the grain size, e.g. the smaller the size, the faster the process. In $L_\alpha$ is also included the temperature dependence of the process (Rutter, 1983).

Lehner and Leroy (2004) reported a similar formulation of the Fick’s law:

$$
J_{gb}^r = -\rho f L_{gb} d \mu / dr
$$

where $J_{gb}^r$ represents the radial component of the diffusive mass flux of dissolved material averaged over a grain boundary thickness $\delta$, $\rho f$ represents the fluid density, and $\mu$ is the mass-specific chemical potential of the solute component in the grain boundary solution phase. $L_{gb}$ represents a phenomenological mobility coefficient. If the solution is diluted enough, the equation can be rewritten in terms of solute mass fraction $C$:

$$
J_{gb}^r = -\rho f D_{gb} dC / dr
$$

(4.2)

where $D_{gb}$ is a constant mass diffusivity through the grain boundary and is approximately equal to $L_{gb} (d \mu / dC) \approx L_{gb} \kappa T / \rho s \Omega s C$, where $\kappa$ represents the Boltzmann constant and $\Omega s$ the molecular volume of the solid.

Local equilibrium across the flat interface follows Gibbs’ equations (Lehner and Leroy, 2004):

$$
\mu^s - T s^s + p / \rho^s = \mu
$$

(4.3)

where $\mu^s$ and $s^s$ are the specific internal energy and entropy of the pure solid phase, $p$ is the pressure in the solution phase and $\mu$ is the chemical potential of the solute component in the solution phase.

At the solid side of the interface, because $-p$ must equal the normal stress $\sigma_n$, equation 4.3 can be rewritten by using the Helmholtz’ free energy term $f^s = \mu^s - T s^s$ Lehner, 1995; Lehner and Leroy, 2004:

$$
f^s - \sigma_n / \rho^s = \mu
$$
Similarly, Rutter (1983) reported:

\[ \mu_{\alpha}^\beta = U_{\alpha} - TS_{\alpha} - \sigma_n V_{\alpha} \]

which expressed the existence of a relationship between the local interfacial normal stress \( \sigma_n \) and the local chemical potential \( \mu_{\alpha}^\beta \). \( U_{\alpha}, S_{\alpha} \) and \( V_{\alpha} \) represent the molar internal energy, entropy and volume of the solid over a stressed surface respectively.

Paterson (1995) described the same local equilibrium in terms of molar volume:

\[ \mu = f^\alpha + \sigma_n V_m \]

An extensive review on the thermodynamics of intergranular pressure-solution is included in Rutter (1983), Lehner and Bataille (1985), Paterson (1995), Lehner and Leroy (2004), and Gratier et al. (2013).

### 4.2.1.1 The nature of the fluid interface

During PSC, minerals dissolve and solutes diffuse along grain boundaries. The structure and thickness of the fluid interface strictly controls the kinetics of the process, lowering the diffusion coefficient by up to two orders of magnitudes (Dysthe et al., 2002). Several models have been proposed to describe the entrapped fluid phase along
4.2 Theoretical background

the grain-boundary.

In the first model, called the *thin-film model*, the material dissolves along an interface boundary or a loaded grain boundary and then diffuses along a continuous fluid film between the grains (Figure 4.2 a) (Hickman and Evans, 1995; Den Brok et al., 2002). The thickness of the fluid film can vary from 10 to 100 nm (Gratier et al., 2013). In the *island-channel structure* model, the interface is represented by a dynamic interconnected network of fluid-filled channels (Figure 4.2 b) (Spiers et al., 1990; Schutjens and Spiers, 1999). In this model, the structure remains in a steady-state but islands and channels continuously change positions (Den Brok, 1998). Similar to the island-channel model, but a static structure, is the *Gratz model* or the so-called *island-crack* model (Figure 4.2 c) (Gratz, 1991; Den Brok, 1998). In this model, the grain boundary interface is characterized by a rough surface, composed by micrometric islands and formed by cracking and subsequent etching of the cracks along the grain boundaries. Stress corrosion causes cracking at the tips, generating new cracks and creating a grain-boundary plumbing network (Gratz, 1991; Den Brok, 1998). Once formed, the micro-asperities remain located where the microcracks meet the interface: for this reason, the model is called the *island-cracks* or *static island-channel* model. Den Brok (1998) conducted experimental studies on deformed quartzites to prove the Gratz model. The results showed that PSC in combination with stress corrosion microcracking (SCM) is the main deformation mechanism occurring in the samples, with important observations:

1. The strain rate is proportional to $1/d$ and not $1/d^3$, where $d$ constitutes the average grain diameter;

2. PSC and SCM are related each other;

3. The differences in the fluid interface can lead to 10 orders magnitude difference in the predicted strain rate (Gratz, 1991).

4.2.2 Experimental studies

In the past 40 years, many experimental studies have been conducted to fully understand the kinetics and thermodynamics governing PSC. These studies aimed to reproduce pressure-solution processes in a lab environment, by compacting and injecting fluids into different rock-analogue materials. Before being described by Rutter (1983), PS was also observed by Sprunt and Nur (1976), Boer et al. (1977), and Sprunt and Nur (1977). Boer et al. (1977) investigated the influence of pressure solution in quartz sand in a number of experiments, and the interplay between
temperature and water content. In the case of lower temperatures, water (1 M NaCl solution) seemed to become the predominant factor in controlling the continuation of the process. PS in sandstones (Sprunt and Nur, 1976) can lead to a porosity reduction up to 50\%, in the presence of distilled water and at temperatures of 270° C - 280° C.

Spiers et al. (1990) studied PSC of rock-salt through uniaxial load of NaCl grains infiltrated by brine saturated solution, and he found that the presence of brine dramatically increased the rate of the pressure-solution process, similar to what reported by Boer et al. (1977) for quartz sand and water. As mentioned before, the rate of the pressure-solution process is very slow in carbonates, so most of the experimental studies have been conducted in materials that provide fast creep rates, like NaCl, KCl, K$_2$CO$_3$ as reported by Spiers et al. (1990) and Gratier (1993), but also in mixtures of halite and phyllosilicates (Bos et al., 2000b; Bos and Spiers, 2001; Renard et al., 2001), and quartz (Cox and Paterson, 1991). Furthermore, the PSC rate limiting step in NaCl is transport, e.g. diffusion controlled, and it is temperature independent (Spiers et al., 1990; Spiers and Brzesowsky, 1993; Gratier et al., 2013) (cfr. section 4.2).

However, Den Brok et al. (1999) raised the problem that NaCl deforms plastically at very low differential stresses and at room P-T conditions: on this basis, crystal plasticity might play a critical role in directing PSC in salt. Den Brok et al. (1999)
performed the same compaction experiments of Spiers et al. (1990) but on NaClO$_3$, to determine if crystal plasticity occurred in experimentally deformed halite experiments and if it played a key role. As Den Brok et al. (1999) explained, this material is a very soluble salt, but it has an elastic-brittle behaviour at room P-T conditions: crystal plastic deformation occurs when the axial stresses are up to 21 MPa. Although the two salts have different rheology at room P-T conditions, the results showed similarity in PSC compaction behaviour testifying that crystal plasticity does not contribute to PSC in NaCl.

The experimental studies reported by Spiers et al. (1990) suggest that creep in rock-salt occurred by diffusion controlled pressure-solution, and that the fluid interfaces resemble an island-channel structure (see section 4.2.1.1). Hickman and Evans (1995) conducted similar experiments, in which halite lenses were compressed against flats of fused silica in brine, to study the kinetics of the pressure-solution process. The results showed a critical increase in the PSC rates at the intergranular boundary between different phases and in the presence of intergranular clays. These results suggest that the presence of different material and insoluble phases, like phyllosilicates and clays, favours the process and accelerates the dissolution rates (Heald, 1959; Rutter, 1983; Hickman and Evans, 1995; Bos et al., 2000a; Bos and Spiers, 2000, 2001; Renard et al., 2001; Gratier et al., 2015). In the presence of phyllosilicates, PSC is accelerated due to a mechanical effect, as biotite is less competent, therefore is weaker than other materials such as quartz or carbonates (it also depends on the grain size) (Niemeijer and Spiers, 2006). A similar conclusion was reached by Renard et al. (2001): clays mechanically enhance PSC by strengthening open grain contacts. In contrast to Spiers et al. (1990) and Schutjens and Spiers (1999), these results do not show evidence for the presence of a island-channel structure fluid interface, but rather a semi-continuous fluid film, along which transport properties have a key role in controlling the kinetics of the pressure-solution process (see section 4.2.1.1).

In recent years, PSC has been further investigated in relation to the mechanics and microstructural evolution of fault rocks. Experimental studies have shown that fluid-assisted deformation mechanisms are likely to allow fault healing under hydrothermal conditions (Hickman and Evans, 1995; Bos and Spiers, 2000). The studies of Hickman and Evans (1995) have important implications for this matter: PSC could lead to a reduction in fault strength and acceleration of the rates at which high fluid pressures are generated in seismogenic zones, lowering the principal stresses and allowing seismic failure at lower stresses. Amongst fluid-rock deformation mechanisms, PSC seems to play an important role in controlling fault healing in interseismic quiescence by increasing grain contact areas and by gouge compaction (Bos et al., 2000b), or by cementing grains (neck growth) (Hickman and Evans, 1995).
The presence of phyllosilicates, more generally clays, inhibits neck growth but strongly increases the rate of pressure-solution, increasing pore fluid pressures and resulting in fault weakness (Bos and Spiers, 2000). To understand the effect of PSC on fault strength and the effect of phyllosilicates on fault healing, Bos and Spiers (2000) and Bos et al. (2000b) conducted a series of rotary shear experiments to further investigate the process. Their studies showed that the presence of clays in halite aggregates significantly reduces fault healing, inhibiting grain contact areas and leading to the development of a clear foliation.

The previous studies are limited to a 2D characterization of the pressure-solution properties. In 2004, Renard et al. (2004) applied Synchroton X-ray microtomography to image the 3D geometry of halite aggregates undergoing compaction driven by pressure-solution. A mixture of sieved NaCl (100-150 µm grain size) was firstly brine saturated then uniaxially compacted with a constant load of 1.3 to 6.3 bars for 7 days. Grain contacts were imaged, permitting mapping of the evolution of grain boundaries: during ongoing deformation, contact healing occurred and the thickness of grain boundaries decreased. A porosity network was extracted, on which permeability was measured. They concluded that the decrease in permeability could have been caused by grain indentation and pressure-solution: contact healing reduced the pore space, while precipitation of new material in free surface areas closed pore throats, strongly modifying fluid pathways.

Thiemeyer et al. (2015) imaged and characterized halite grains, and fluid inclusions trapped in natural rock salt through micro- and nano-tomography. In particular, Thiemeyer et al. (2015) showed that there is no correlation between the pore space and the distribution of anhydrite aggregates, suggesting that anhydrite is not responsible for macro-porosity formation, which was instead generated by a complex deformation history.
4.2 Theoretical background

4.2.3 Stylolites

The localisation of pressure-solution processes often causes the formation of characteristic features called **stylolites**. Stylolites are localised dissolution surfaces, sutured and decorated with a mixture of clays, organic material and oxides. They form predominantly in low-pressure metamorphic and diagenetic conditions (Rutter, 1983) and they are present in many lithologies (Park and Schot, 1968). Stylolites are especially common in carbonates, including both limestones and dolomites (Carrio-Schaffhauser et al., 1990; Karcz and Scholz, 2003; Renard, 2004; Evans and Elmore, 2006; Hassan, 2007; Ebner et al., 2009, 2010b), but also occur in quartzites (Heald, 1955; Gratier et al., 2005; Weibel and Keulen, 2008), sandstones (Heald, 1955) and mudstones (Ebner et al., 2009). Stylolites were first recognized by Stockdale (1922), who associated their formation with pre-existing structures, like joints or bedding-parallel surfaces, but their nature can also be associated with tectonic processes (Gratier, 2003). During the formation of stylolites, the dissolution process can remove approximately 50% of the original rock (Fletcher and Pollard, 1981; Aharonov and Katsman, 2009), causing important changes in the porosity distribution, mineral composition and texture of the rock. This process induces chemical and physical alterations, causing changes in fluid flow and solute transport.

The geometry of stylolites is characterized by 3D interlocking and highly indented teeth of the wall rock (Passchier and Trouw, 2005) (Figure 4.3). Localised pressure-solution acts on one side of the surface, roughening it, while on the other side a concentration of non-soluble phases develops (Passchier and Trouw, 2005). Stylolite roughness can range over several scales (from micron- to decimeter-scale) (Ebner et al., 2010a; Gratier et al., 2013). The origin of this roughness has been investigated through different experimental and numerical modelling studies, as it is recognised to be important to estimate stress values through the direction of the teeth (Ebner et al., 2009, 2010a; Gratier et al., 2013), or to record the compaction history of the rock and dissolved material through the teeth amplitude (Koehn et al., 2007, 2012).

Two main models regarding stylolite nucleation and propagation have been developed. Fletcher and Pollard (1981) analysed stylolites theoretically through a model where the host rock is represented by a homogeneous, isotropic and linearly elastic material. A thin lamina of material from the unloaded elastic medium is cut to simulate a pre-existing crack. The formation of a solution surface is achieved by applying a load perpendicularly to the surface. The shear perturbation induced by the load is accommodated by opening mode I cracks, in which the signs of displacements and stresses have changed. For this reason, the model is called “anticrack theory” and stylolites are nucleated by a self-localizing pressure-solution process.
Aharonov and Katsman (2009), using a spring network model, simulated stylolite propagation either with pressure solution and clay enhancement acting alone, or acting in combination. The elasticity in the model follows Hooke’s law. Their simulations showed that the stress is not sufficient to allow the propagation of stylolites. Laronne Ben-Itzhak (2011) tested the numerical models of Aharonov and Katsman (2009) and rejected the anticrack theory. According to the simulations, the propagation of stylolites should include the effect of clay enhanced dissolution: pressure-solution acts on the tips to let the stylolite grow, while clay enhanced dissolution acts on the sides, thickening the stylolite but without elongating it.

A similar model to Aharonov and Katsman (2009), based on a stochastic equation was proposed by Renard (2004) to explain the 3-dimensional architecture of stylolites. According to the model, long-range elastic local stress fluctuations roughen the surface, while surface tensions acting along the interface smooth it. Moreover, the tips of stylolites are particularly important as they control transport properties around the stylolite. The study of stylolite tips through X-ray tomography led Carrio-Schaffhauser et al. (1990) to notice a strong decrease in the X-ray attenuation values in the areas surrounding stylolites, where no clay dissolution seam was present. Carrio-Schaffhauser et al. (1990) noticed that the decrease in X-ray attenuation values was
4.2 Theoretical background

related to a strong increase in the porosity content. This volume was identified as process zone, and it holds particular importance with regards to porosity and permeability evolution during stylolite growth.

The enhanced effect of clays and phyllosilicates on the localisation of pressure-solution processes has been investigated over a number of studies. Different effects have been proposed and Laronne Ben-Itzhak (2011) summarised them:

- The presence of smaller grain contacts, which provide higher surface areas, can inhibit cementation of the grains and contact healing (Zubtsov et al., 2004).

- Other models proposed that the increase creep rates in the presence of clays are attributed to the presence of an increase electrochemical potential between dissimilar phases (Aharonov and Katsman, 2009; Greene et al., 2009).

- Another cause may be related to the intrinsic different mechanical behaviour of the clays/phyllosilicates grains undergoing compaction. When loaded under stress, these materials deforms much faster than other material (i.e. NaCl or carbonates), therefore allowing a localisation of the process along the interfaces (Thiemeyer et al., 2015).

- Weyl (1959) and Renard et al. (2001) proposed that the localisation of the process is related to enhanced Thin-Film diffusion effect. The diffusion rates in the water film is much higher due to the presence of water films surrounding each clay particle.

It remains unclear which mechanism is responsible for the enhanced effect.

4.2.4 Strain shadows and strain caps

Other microstructures related to PSC are strain shadows and strain caps. Strain shadows (e.g. pressure shadows) have been extensively studied in the literature (Pabst, 1931; Choukroune, 1971; Beutner and Diegel, 1985; Etchecopar and Malavieille, 1987; Kanagawa, 1996; Hilgers and Urai, 2002). However, strain caps are not well described and their formation is unclear. According to Passchier and Trouw (2005), strain shadows and strain caps represent strain partitioning domains around core objects. Generally, strain shadows form on the both sides of the object, whereas strain caps form on the quarters opposite to the strain shadows and they are enriched in insoluble minerals such as micas and clays (Passchier and Trouw, 2005; Abu-Alam and Stüwe, 2011). They can form in response to different mechanisms, in some cases as response to solution mass transfer mechanisms. If this is the case, strain caps represent the site at higher stresses where dissolution occurs, while the strain shadows represent
the site at lower stresses where precipitated material is present (Figure 4.4) (Passchier and Trouw, 2005).

Part of the experimental work described in this thesis has been performed with the aim of studying this phenomenon. Over time, µCT is able to capture the evolution of the pore space in the quarter orthogonal to the uniaxial load where strain caps should develop and where the phyllosilicates wrap around the glass beads. In this way, although the resolution might be insufficient to identify the reprecipitation sites, µCT will still be able to monitor the formation and evolution of strain caps in four dimensions, providing new insights on the formation mechanisms.

Figure 4.4: Illustrative sketch of strain shadows and strain caps. From Passchier and Trouw (2005).
4.3 Experimental procedure

Experiments were performed with different sample compositions to monitor their effect on the pressure-solution process and on the dynamic evolution of porosity and pore connectivity. A tabulation of all types of experiments, including scanning parameters, is presented in Table 4.1. Compaction durations of the experiments changed over time as earlier (and shorter) experiments were needed to understand the extent and outcomes of the process, and to refine future experiments in sample preparation and/or sample loading. Samples loaded at 1.66 MPa were not analysed extensively as they do not show substantial reduction in porosity nor strong degrees of grain indentations. In the case of pure NaCl and NaCl-biotite samples, two experiments were performed to produce repeatability of the data and comparability. Samples loaded at 6.64 MPa were extensively analysed following the workflow reported in chapter 2, section 2.5.3.

Each sample vessel was first loaded for 10 minutes to produce an aggregate material. Successively, the sample vessel was unloaded, positioned on the rotary stage and scanned. After each scan, the sample vessel was re-positioned under the loading frame and compacted till the next scan. For each sample, I took from 10 to 12 microtomographic scans during the duration of the whole experiment. Details of the experimental setup are explained in chapter 2, section 2.5.1.
<table>
<thead>
<tr>
<th>Sample type</th>
<th>Sample mass</th>
<th>Uniaxial load</th>
<th>Compaction time</th>
<th>Scan conditions</th>
<th>Spatial resolution [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure NaCl</td>
<td>0.18 g</td>
<td>1.66 MPa</td>
<td>208 hs</td>
<td>100 KeV</td>
<td>9</td>
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<td></td>
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<td></td>
<td></td>
<td>2.8 W</td>
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<td></td>
<td>1500 proj.</td>
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<td>4 frames averaged,</td>
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<td></td>
<td>0.5 s</td>
<td></td>
</tr>
<tr>
<td>Pure NaCl</td>
<td>0.18 g</td>
<td>1.66 MPa</td>
<td>231 hs</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>NaCl-kaolinite</td>
<td>0.136 g NaCl</td>
<td>1.66 MPa</td>
<td>231 hs</td>
<td>7</td>
<td></td>
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<tr>
<td></td>
<td>0.045 g kaolinite</td>
<td>1.66 MPa</td>
<td>231 hs</td>
<td></td>
<td></td>
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<tr>
<td>Pure NaCl</td>
<td>0.18 g</td>
<td>6.64 MPa</td>
<td>231 hs</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>NaCl-glass beads</td>
<td>0.11 g NaCl</td>
<td>1.66 MPa</td>
<td>441 hs</td>
<td>6</td>
<td></td>
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<td></td>
<td>0.028 g GB</td>
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<tr>
<td>NaCl-glass Beads</td>
<td>0.11 g NaCl</td>
<td>6.64 MPa</td>
<td>437.5 hs</td>
<td>6</td>
<td></td>
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<tr>
<td></td>
<td>0.028 g GB</td>
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<tr>
<td>NaCl-biotite</td>
<td>0.10 g NaCl</td>
<td>6.64 MPa</td>
<td>444 hs</td>
<td>6</td>
<td></td>
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<td></td>
<td>0.02 g Bt</td>
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<tr>
<td>Pure NaCl</td>
<td>0.18 g</td>
<td>6.64 MPa</td>
<td>2446.5 hs</td>
<td>6.5</td>
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<td>70 keV</td>
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<td>2.8 W</td>
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<td>2000 proj.,</td>
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<td></td>
<td>2 s</td>
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<tr>
<td>NaCl-biotite</td>
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<td>2455 hs</td>
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</tr>
<tr>
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<td>0.02 g Bt</td>
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</tr>
<tr>
<td>NaCl-biotite-glass beads</td>
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<td>2465 hs</td>
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</tr>
<tr>
<td></td>
<td>0.03 g Bt</td>
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<td></td>
<td>0.02 g GB</td>
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</table>

Table 4.1: Tabulation of the experimental conditions for each the experiments performed.
4.4 Results

4.4.1 Data description

4.4.1.1 Pure NaCl

A control experiment was performed with a pure NaCl sample, in order to test the experimental equipment and to establish the behaviour of NaCl in the absence of biotite and glass beads. In this test, a sample of pure NaCl was compacted and the dynamic evolution of porosity was monitored by acquiring µCT scans at regular interval times (Table 4.1). Working conditions are reported in Table 4.1. The sample mass was 0.18 g, and the applied uniaxial load was 1.66 MPa. The sample was compacted for 208 hours, which led to 25 % vertical shortening (in Figure 4.5 A the compaction curve is presented in red).

This experiment showed that the experimental setup was suitable to investigate the pressure-solution process. The frames allowed deformation of the sample with a constant uniaxial load, and the vessel proved to be suitable for X-ray imaging, which allowed monitoring of the progressing decrease in pore space and grain rearrangement over time. However, during the experiment, porosity only decreases by ~10 %, leaving the sample with ~30 % porosity (Figure 4.6). In this control experiment, a first attempt was made to analyse the evolution of NaCl grains. NaCl grains were segmented and separated, successively labelled and label analysis was then applied (cfr. chapter 2 and section 2.5.2 and 2.5.2.3). However, it appeared that the application of simple shape analysis (e.g. surface area to volume ratio) is highly sensitive to the applied segmentation method, so it cannot be used to establish whether grains have been deformed or dissolved (see chapter 2, section 2.5.2.4 and Figure 2.26, Figure 4.7). There is no image criteria allowing separation of the grains when they are in close contact to each other. For this reason, in the other experiments digital image analysis of µCT data was combined with 3D-DIC (cfr. chapter 2, section 2.3, Figure 2.9), to monitor the evolution of grains with increasing compaction, while the pore space was analysed with image analysis as explained in chapter 2, section 2.5.2.

Three more experiments were performed with pure NaCl samples: one loaded at 1.66 MPa and two at 6.64 MPa, to determine the effects of different loads on the process. The duration of each experiment varied (Table 4.1). The sample loaded at 1.66 MPa experienced 48 % vertical shortening over 231 hours. The samples loaded at 6.64 MPa experienced 31 % vertical shortening over 227 hours, and 25 % over almost 2446.5 hours of compaction, respectively. The sample loaded at 1.66 MPa
Figure 4.5: A) Compaction curve for pure NaCl samples. The compaction curve for the preliminary experiment used to test the experimental setup is given in red. B) The curves are plotted by removing the effect of the first 20 hours of compaction due to the initial grain packing: vertical shortening has been calculated from the time step relative to 20 hours of compaction. "1st" and "2nd" indicate the first and second experiment for the same sample composition, respectively.

experiences a greater vertical shortening because the initial packing of the grains was looser compared to the other samples.
4.4 Results

Figure 4.6: Vertical μCT slices of control experiment: A) 11 % vertical shortening, B) 25 % vertical shortening.

Figure 4.7: Analysis of preliminary experiment: Surface area to volume distribution for increasing deformation [%]. There is no clear distinction in shape with increasing deformation. Shape analysis are highly sensitive to the segmentation method applied, and cannot be used alone to discriminate between deformation processes, as it might introduce errors into the analysis.

In Figure 4.5 A, the curves are reported for the NaCl experiments. The compaction curves are characterised by a gradually decreasing slope with increasing
compaction time. The first compaction hours (5-23 hours) are characterised by a very steep gradient, while successively the slope gradually decreases in the second part of the compaction. A close up image is presented in Figure 4.5 B, where the curves are plotted by removing the effect of the first 20 hours of compaction: vertical shortening has been calculated from the second compaction step, after 20 hours of loading. The curves follow the same trend over time, indicating repeatability of the data.

From the vertical µCT slices, it is evident that the sample loaded at 1.66 MPa retains \(\sim 30\%\) porosity compared to the sample loaded at 6.64 MPa, which retain \(\sim 20\%\) after the same compaction time (Figure 4.8 A, B). In the longest experiment, porosity was reduced by \(\sim 30\%\) over time, and grains presented high degrees of indentations, as shown by the arrows in Figure 4.8 C. These indentations represent grains (NaCl in this case) indenting each other at high angle, and which started losing their original cubic shapes. Results of data analyses are reported in section 4.5.
4.4 Results

Figure 4.8: Vertical μCT slices of pure NaCl samples showing the evolution of the samples with increasing vertical shortening (in percentages): A) 1.66 MPa, 231 compaction hours; B) 6.64 MPa, 227 hours; C) 6.64 MPa, 2446.5 hours. White arrows indicate high degrees of indentations.
4.4.2 NaCl-biotite/NaCl-kaolinite

Three experiments with phyllosilicates and clays were performed: two samples of NaCl grains were mixed with biotite grains, and loaded at 6.64 MPa; one was mixed with sieved kaolinite grains, and loaded at 1.66 MPa (Table 4.1). In the longest experiment (2455 hours of compaction), biotite was mixed with NaCl and pre-localised in a central layer, to avoid clogging of biotite particles in the fluid connection (cfr. chapter 2, section 2.5.1.4).

The sample containing kaolinite experienced 29% vertical shortening over 231 hours of compaction (Figure 4.9 A). The samples loaded at 6.64 MPa experienced 39 % vertical shortening over 444 hours, and 35 % over 2455 hours, respectively (Figure 4.9 A). As for the pure NaCl samples, the sample in the longest experiment compacted to a lesser extent and at a slower rate, compared to the other two samples. The compaction curves for these mixed materials are also characterized by a gradually decreasing slope, as for the pure NaCl samples.

In Figure 4.9 B, the curves are plotted by removing the effect of initial grain packing, and the vertical shortening has been measured from the time step relative to 20 hours of compaction. The curves follow the same trend, and have the same slope. Furthermore, the samples reached a higher vertical shortening compared to the pure NaCl samples. In the longest run ("NaCl-biotite 2nd"), the curve is characterized by increasing slope towards the end, similar to the NaCl and NaCl-biotite-glass samples (Figure 4.9 B).

Visual comparison of the vertical µCT slices clearly shows that the presence of biotite induced a considerable reduction in porosity, and greater degrees of indentation between NaCl grains, which lost their original cubic habit (Figure 4.10). In the sample which was compacted for 444 hours, however, crushed and sieved biotite grains were thin enough to have a greyscale value very close to that of the NaCl, and consequently were no longer visible as discrete flakes after extensive compaction (Figure 4.10 A). This is the reason why in the longer experiment biotite was prepared following a different method, as explained in chapter 2, section 2.5.1.3: in this sample, biotite flakes were visible and they could be distinguished clearly from the NaCl grains even after considerable compaction (Figure 4.10 B).
4.4 Results

Figure 4.9: A) Compaction curves for the NaCl-biotite/kaolinite samples. B) The curves are plotted by removing the effect of the first 20 hours of compaction due to the initial grain packing: vertical shortening has been calculated from the time step relative to 20 hours of compaction. In these sample, the layer of biotite was pre-localised in the central layer, to avoid clogging of the biotite particles (cfr. chapter 2, section 2.5.1.4). "1st" and "2nd" indicate the first and second experiment for the same sample composition, respectively.
Figure 4.10: Vertical μCT slices of NaCl-biotite samples. Vertical shortening is reported in percentage. A) NaCl-biotite, 6.64 MPa, 227 hours: sieved biotite grains are not as easily recognizable; B) NaCl-biotite, 6.64 MPa, 2455 loading hours: only the experiment with biotite flakes (in white) shows all materials clearly. White arrows indicate areas of reduced porosity, where NaCl grains indent more, losing their cubic habit, and/or precipitation sites.
4.4 Results

4.4.3 NaCl-glass beads

Two experiments in glass beads were performed, at different loads, but compacted for the same duration (Table 4.1). A mixture of NaCl and glass beads (20 % mass, 0.5 mm diameter) was loaded in a cell at 1.66 MPa: mass of NaCl was 0.11 g, and mass of glass beads was 0.028 g. The same proportion of material was loaded in a second cell at 6.64 MPa, to monitor the effect of a bigger load for the same material. Vertical shortening of the samples was as follows: i) 15 % NaCl-glass beads (1.66 MPa); ii) 32 % NaCl-glass beads (6.64 MPa) (Figure 4.11 A). The compaction curves show a progressive decrease in the gradient with time, which also occurs in the other samples. Furthermore, as it happened for the NaCl-biotite samples, the PSC was favoured in the presence of a bigger uniaxial load (Figure 4.11 A). Grains showed stronger degrees of indentations and a substantial reduction of pore space (~ 15 %) in the sample loaded at 6.64 MPa, compared to the samples under the smaller load, which showed no significant change in porosity content (Figure 4.12 A, B, see section 4.5.1).

4.4.4 NaCl-glass beads-biotite

In another sample, NaCl grains were mixed with glass beads and biotite to monitor the combined evolution of biotite and NaCl grains with regards to the glass beads. 0.03 g biotite (20 % by mass) were heterogeneously mixed with 0.02 g glass beads (15 % by mass) and with 0.12 g NaCl (Table 4.1). The sample was prepared following a wet loading method (cfr. chapter 2, section 2.5.1.4). The sample was loaded to 6.64 MPa, and compacted for 2465 hours. The final vertical shortening was 26 % (Figure 4.11 A).

The vertical shortening was also recalculated by removing the effect of initial packing in the first 20 hours of compaction, as for the previous experiments (Figure 4.11 B). The graph shows that the NaCl-glass-biotite sample compacted more than the NaCl-glass beads and pure NaCl samples, but less than NaCl-biotite samples.

The sample showed progressively higher degrees of grain indentations between NaCl-biotite interfaces and NaCl-glass interfaces; biotite flakes progressively wrapped around the NaCl and beads forming strain caps (Figure 4.12 C, see section 4.6.4). The pore space was critically reduced in the presence of biotite (~ 20-25 % from the original content), as it occurred in NaCl-biotite samples (Figure 4.12 C, see section 4.5.1). Pore sizes strongly decreased over time, and the former shapes of NaCl grains were not preserved.
**Figure 4.11:** A) Compaction curves for NaCl-glass beads and NaCl-glass beads-biotite. The amount of vertical shortening experiences by the NaCl-glass beads-biotite sample is lower than in NaCl-glass beads, probably due to a different initial packing of the grains, as shown in B. B) The curves are plotted by removing the effect of the first 20 hours of compaction due to the initial grain packing: vertical shortening has been calculated from the time step relative to 20 hours of compaction. The NaCl-glass beads-biotite sample now shows a higher vertical shortening than the NaCl-glass beads samples and pure NaCl samples, whereas it compacts less compared to the NaCl-biotite sample. “1st” and “2nd” indicate the first and second experiment for the same sample composition, respectively.
4.4 Results

Figure 4.12: Vertical µCT slices of the NaCl-glass beads samples (A, B), and NaCl-glass beads-biotite sample (C). Note the progressive and substantial reduction in pore space in the sample containing biotite flakes (white). Glass beads shown in darker grey colour. White arrows indicate areas of reduced porosity between NaCl and biotite grains; green arrows indicate biotite flakes wrapping around NaCl grains and beads.
Chapter 4. Pressure-solution processes

4.5 Results of digital image analysis

Digital image analysis was conducted on subvolumes of $400^3$ voxels extracted from the original µCT (cfr. chapter 2, section 2.5.1, section 2.5.2.2).

4.5.1 Bulk porosity

Bulk porosity analyses were performed following the procedure described in section 2.5.2 and only on the samples loaded at 6.64 MPa. The samples loaded at 1.66 MPa showed a lower reduction in porosity, and fewer grain indentations, indicating that PSC processes might not be fully active; therefore only the samples loaded at 6.64 MPa were analysed. Error bars were calculated from eroded (lower bar) and dilated data (upper bar), following the approach described in chapter 2, section 2.4.3 and 2.5.3. Errors introduced by the segmentation/separation methods are discussed in section 4.6.7, as well as in chapter 5, sections 5.1, 5.1.2. Furthermore, the accuracy of the segmentation method was also evaluated by using measurements calculated in Avizo® from a scan of a volume of NaCl of known mass. The weighted mass was used to determined the porosity within the sample. The same porosity was then calculated from the segmented pores of the µCT data. The calculated and tomographically analysed volumes were equal, within 0.001 cm$^3$ over 0.03 cm$^3$ of volume.

4.5.1.1 Pure NaCl

In the shortest experiment, the NaCl sample experienced a total 15% porosity decrease over 227 hours (Figure 4.16 A). The error bars reduce from ±14 % to ±12 % with increasing deformation (cfr. section 4.6.7). Most of the pore space reduction was accommodated between 17 % and 26 % vertical shortening, whereas there was only a 2 % porosity decrease in the last 161 hours.

In the longest experiment, NaCl sample showed 20 % decrease in bulk porosity over 2446.5 hours (Figure 4.16 D). Pore space decreased linearly over time. Error bars reduced from ±11 % to ±7 % with increasing deformation.

4.5.1.2 NaCl-biotite

In the sample compacted for 444 hours, the pore space was reduced by 26 % (Figure 4.16 C). In this case, most of the deformation was accommodated equally between the very first hours of compaction and the last 351 hours of compaction. Error bars reduced from ±12 % to ±6 % with increasing deformation.

In the sample loaded for 2465 hours, porosity was reduced by ~18 % (Figure 4.16 E).
4.5 Results of digital image analysis

However, contrary to what happened in the pure NaCl samples, the pore space was reduced heterogeneously within the sample. Porosity reduction was partitioned into the biotite central layer and the marginal NaCl layers (section 4.5.1.3). Error bars equal to ±11% at 17% vertical shortening, however, with increasing compaction, the errors are not homogeneous and they show +8% and -4% at 35% vertical shortening (cfr. section 4.6.7).

4.5.1.3 Porosity distribution and strain partitioning within the sample

Measurements of the biotite layer thickness for increasingly shortened dataset indicated a progressive reduction from 1.77 mm to 0.9 mm over 2455 hours of loading (Figure 4.13 A). The reduction in biotite layer thickness was accompanied by a strong reduction of the pore space: from 11% to almost 1% relative to the chosen subvolume (Figure 4.13 B, section 4.5.1.3). To better understand how bulk porosity evolved throughout the sample, the pore space for each horizontal slice was calculated and plotted against the vertical loading axis z, for increasingly deformed datasets. The measurements were performed on the pure NaCl and NaCl-biotite samples loaded at 6.64 MPa for 2465 hours: they showed strong differences in the vertical porosity distribution. While the pure NaCl showed a homogeneous decrease in porosity content within the sample for increasing deformation (Figure 4.14 A), the sample NaCl-biotite showed a substantial decrement of porosity within the central biotite layer, which approached 0% porosity content (Figure 4.14 B). This indicates that porosity reduction was partitioned differently into the biotite central layer and the NaCl marginal layers. Visualisation of a subvolume within the central layer in Figure 4.15 shows how pores were progressively removed and biotite flakes progressively localized and aligned with increasing compaction.

Porosity reduction reflects also strain partitioning between the biotite and the NaCl layers (Figure 4.13 C). Measurement of the biotite and NaCl layers thickness allowed identifying how the strain was accommodated differently in these layers. In the first compaction hours, the steep gradient of the biotite layer indicates that strain was mostly accommodated by the biotite. Successively, deformation was accommodated by the marginal NaCl layers which show an increase in the gradient curve compared to the biotite, which indeed reaches steady-state between 208 and 1208 hours of compaction (Figure 4.13 C). In the last increment of deformation, the gradient of the biotite curve increases again, while the gradient of the marginal NaCl layers nearly stabilises.

Comparison with compaction curves of different sample compositions shows that in the case of a pure NaCl sample, strain was accommodated linearly, whereas
Chapter 4. Pressure-solution processes

Figure 4.13: Graphs showing the evolution of biotite thickness (A), porosity (B) and strain partitioning (C-D) in NaCl-biotite sample with increasing compaction and vertical shortening [%]. A) Thickness evolution of biotite layer with increasing vertical shortening. B) Porosity evolution in the central biotite layer with increasing deformation, in relation to the chosen subvolume (400^3 voxels) and to the central biotite subset. C) Strain partitioning in the biotite central layer and NaCl marginal layers. Compaction duration (hours) is reported as logarithmic scale. D) Strain partitioning with reference to compaction curves for other sample compositions. Compaction duration (hours) is reported in logarithmic scale.

in the marginal NaCl layers of the NaCl-biotite sample strain partitioning was nonlinear, and it reflected the accommodation of strain in the biotite layer (Figure 4.13 D). This might be related to an enhanced dissolution mechanism in biotite-rich layers, which leads to fluids supersaturation. This in turn inhibits pressure-solution in the more marginal NaCl layers in the samples, and the fluid phase allows communication between all the regions of the samples.
4.5 Results of digital image analysis

**Figure 4.14:** Porosity as a function of the vertical loading axis z for increasing strain [%]: A) Pure NaCl sample; B) NaCl-biotite sample.

**Figure 4.15:** 3D renderings of a subvolume from the sample NaCl-biotite in the last experiment for increasingly shortened datasets showing the distribution of pores (blues) and biotite (red): A) 17 %, B) 26 %, C) 35 %. 3D rendering of the distribution of the pore space with increasing deformation: D) 17 %, E) 26 %, F) 35 %.
4.5.1.4 NaCl-glass beads

The sample with mixed NaCl and glass beads experienced a decrease in bulk porosity of 14 % over 444 hours of compaction (Figure 4.16 B). Most of the reduction was accommodated between 16 and 26 % vertical shortening (~ 10 % reduction), with only 4 % decrease in the last 345 hours of compaction (between 26 % and 32 % vertical shortening). Error bars decrease accordingly over time, from ±10 % to ±7 % with increasing deformation.

4.5.1.5 NaCl-glass beads-biotite

In the presence of glass beads and biotite together, the sample showed only 15 % change in bulk porosity over 2465 hours of compaction (Figure 4.16 F). 9 % of this decrease was accommodated between 21 % (207 hours) and 26 % vertical shortening (2465 hours). Error bars show a progressive reduction. However, the error bar at 14 % vertical shortening isn’t equally partitioned between the eroded and dilated data. The lower error bar, given by the eroded data, shows a - 6 % bulk porosity compared to the original volume, while the upper bar, given by the dilated data, shows an increase of 10 %. However, the error bars homogenise with increasing deformation, showing a progressive reduction ±5 % of the total volume (cfr. section 4.6.7).
4.5 Results of digital image analysis

4.5.2 Pore size and shape

Pores were segmented and labelled following the procedure described in chapter 2, sections 2.5.3 and 2.5.3.3. Pores with volume smaller than 10 voxels (2746.25 µm$^3$ assuming 6.5 µm as voxel size) were discarded from pore size distribution analyses, and only pores with volumes larger than 64 voxels were considered for shape analyses (chapter 2, sections 2.5.3 and 2.5.3.3).

4.5.2.1 Pure NaCl

In the first experiment, the major contribution to pore size evolution derived from pores smaller than $3.2 \times 10^4$ µm$^3$ that are created with increasing compaction, and from pores larger than $1.6 \times 10^7$ µm$^3$ which decreased with increasing strain (from 24 to 4) (Table 4.2, Figure 4.17). The cumulative frequency plot shows a significant increase for all pore sizes, except for the larger ones, at 31 % vertical shortening after 227 hours of compaction (Figure 4.19 A, B).

In the second experiment, the major contribution derived always from small pore sizes (Table 4.2). With increasing deformation, small pores ($< 1.3 \times 10^5$ µm$^3$) almost doubled in frequency (192 to 412 in the last compaction). With increasing deformation, larger pores were also affected (Table 4.2). The cumulative frequency plot shows that the major contribution with increasing strain results from intermediate size classes ($10^5$-$10^6$ µm$^3$), while big sizes (volumes $> 10^7$ µm$^3$) did not show a substantial decrease, and they showed little changes from the low strain dataset (Figure 4.19 C, D).

Changes in shapes and orientations with increasing deformation have also been analysed. The Flynn diagrams do not show major changes towards either prolate or oblate pore shapes (see Appendix C, section C.2, Figure C.2 A). The orientation of the inscribed ellipses was plotted as well (see Appendix C, section C.2). Figure C.5 A shows no clustering of the pores in any preferential direction with increasing deformation. Furthermore, shape factor values were also plotted and they do not differ substantially with increasing compaction: most of the pores share common values of three to four shape factor even at the highest degrees of deformation (Figure 4.21 A).

4.5.2.2 NaCl-biotite

The evolution of pore space in the presence of phyllosilicates was significantly different compared to the pure NaCl experiment. In the first experiment, the major
4.5 Results of digital image analysis

Figure 4.17: Evolution of pore size distribution with time and vertical shortening, derived from the label analysis with a lower threshold at 10 voxels for different samples.

contribution to the pore size evolution is given from sizes in range $10^4$-$10^5$ $\mu m^3$ and from pores larger than $10^6$ $\mu m^3$, which dramatically diminished over time (from 1200 to 373) (Table 4.2, Figure 4.17 C, Figure 4.19 E, F). Pore shapes and orientations do not change with increasing compaction (see Appendix C, section C.2, Figure C.1 A, Figure C.4 A).

In the second experiment, the number of separated pores decreased from 2230 to 1516 (Figure 4.17 E), substantially different from the pure NaCl experiment, in which the number of pores decreased by a few (Table 4.2). With increasing deformation, there was a progressive decrement of larger pores ($> 1.6 \times 10^7$ $\mu m^3$, from 10 to 0),
Chapter 4. Pressure-solution processes

and an increase in smaller pores \(< 10^5 \, \mu m^3\), from 447 to 664), compared to the pure NaCl sample (Figure 4.17 E, Table 4.2). Pores in range \(10^6 - 1.6 \times 10^7 \, \mu m^3\) dramatically decreased from 1100 to 343 (Table 4.2). The progressive disappearance of larger pores is testified by the cumulative volumes and frequencies plots (Figure 4.19 G, H), as also observed in the vertical tomographic images (Figure 4.10 C) and 3D renderings. Pores do not evolve in shape or orientation with increasing vertical shortening (Figure C.2 B, Figure C.5 B). However, to distinguish the effect of phyllosilicates and pure NaCl in this sample, the layers were treated separately.

**Biotite layer** A subvolume containing the phyllosilicate layer was extracted for five compaction steps and the pore size distribution measured for increasing deformation (Figure 4.18 B, Table 4.2). Overall, the number of pores decreased from 1143 to 561 with increasing compaction. The curves show an increment in small pores \(< 6.5 \times 10^4 \, \mu m^3\) after the first 17 % vertical shortening (blue curve), but they successively did not vary in frequencies. Significant decrease in frequency was shown by pores in range \(10^6 - 1.6 \times 10^7 \, \mu m^3\), from 534 to 43 with time, while no pores larger than \(1.6 \times 10^7 \, \mu m^3\) survived after 35 % vertical shortening (Table 4.2). Flynn diagrams do not show any change in pore shape with increasing compaction (Figure C.2 C). Shape factor plots indicate that pores approached values closer to one with increasing deformation but they did not show substantial shape change (Figure 4.21 B). Orientation analyses do not show any clustering around specific direction (see Appendix C, section C.2, Figure C.6 A).

**NaCl Layer** With time, the number of pores in these marginal layers decreased from 1124 to 1086, a small decrement similar to the pure NaCl experiment. There was a general decrease in smaller pore sizes \(< 2.6 \times 10^5 \, \mu m^3\), and in larger pores (Figure 4.18 A, cfr. Figure 4.15). The pore size distribution graph resembles the pore size distribution for the pure NaCl experiment. This layer did not show any change in shape and orientation with increasing compaction as it happens for the biotite layer (see Appendix C, section C.2, Figure C.2 D, Figure C.6 B). Although the Flynn diagrams do not show substantial differences in prolate/oblate shapes, the shape factor plot shows a minimal shift towards lower values (more spherical) (Figure 4.21 C). However, this shift is not sufficient to indicate shape changes as the Flynn diagrams did not reveal shape changes.

**4.5.2.3 NaCl-glass beads**

With increasing deformation, the total number of pores increased from 1444 to 1847. This increase was accommodated by the creation of smaller pores \(< 1.3 \times 10^5 \, \mu m^3\), which evolved from 161 to 591 over time, a much larger increase compared to the
4.5 Results of digital image analysis

Figure 4.18: Pore size distribution in central biotite layer (A) and marginal NaCl layers (B) for NaCl-biotite sample in the second run (6.64 MPa).

other experiments (Table 4.2). The compaction also affected larger pores (> $10^6$ µm$^3$), which experienced a progressive decrease, as it occurs in other sample compositions (Figure 4.17 B, Table 4.2). This trend is evidenced by the cumulative frequency plot which shows a marked shift in the curve gradient for volumes smaller than $10^6$ µm$^3$ at 32 % vertical shortening, whereas overall larger pores decreased in frequency (Figure 4.20 A, B). With increasing deformation, the pores showed neither changes in shapes nor a progressively preferential orientation (see Appendix C, section C.2, Figure C.1 B, Figure C.4 B).

4.5.2.4 NaCl-biotite-glass beads

This sample showed a significantly different evolution of the pores compared to the pure NaCl and NaCl-biotite samples. As for the NaCl-glass beads sample, with increasing deformation the number of pores incremented to from 1917 to 2068 (Table 4.2). The majority of deformation was accommodated by pores smaller than $1.3 \times 10^5$ µm$^3$, which increased from 309 to 1014 over time, a much larger increase compared to the pure NaCl sample (Figure 4.20 C, D, Table 4.2). Only six large pores (> $1.6 \times 10^7$ µm$^3$) were present in the less deformed sample and they progressively reduced to one at the end of the experiment (Table 4.2). As for the other samples, pores did not change in shape or orientation with increasing deformation (see Appendix C, section C.2, Figure C.1 C, Figure C.5 C).
Figure 4.19: Cumulative plots for pure NaCl and NaCl-biotite: A,B) Pure NaCl first run; C,D) Pure NaCl second run. E,H) NaCl-biotite second run; G, H) NaCl-biotite second run.
### Table 4.2: Tabulation of pore size evolution for increasing strain and different sample compositions. Grey box highlights the values for the pure NaCl experiments.

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Figure 4.20: Cumulative plots for NaCl-glass beads (A, B), and NaCl-biotite-glass beads samples (C, D).
4.5 Results of digital image analysis

Figure 4.21: Shape factors for pure NaCl (A) and NaCl-biotite samples (B, C): B) central biotite layer, C) marginal NaCl layers.
4.5.3 Interconnectivity

Interconnectivity analyses have been conducted on the labelled pore space from subvolumes of the original data (400$^3$ voxels), following the method outlined in chapter 2, section 2.5.3. As with the pore size analyses, pores smaller than 10 cubic voxels were not considered.

While in the pure NaCl and NaCl-glass beads the pore space remained highly interconnected through the experiments (Figure 4.22 G-I), the samples containing biotite showed a different behaviour (Figure 4.22 D-F and J-M, Table 4.3). In the first run of NaCl-biotite, the presence of biotite affected the pore size distribution within the sample. Where phyllosilicates were present, the pores became smaller and much more disconnected from the main pore volume (Figure 4.22 F). The largest pore cluster accounted for 89.3% of the total pore space and only 8% of the analysed subvolume. The decrease in the degree of interconnectivity is also further illustrated by the increasing number of disconnected pore clusters: with increasing compaction, the number of disconnected pores tripled, from 277 to 880 in the highest degree of deformation.

In the second run, the compaction caused the disconnection of the pore space in two large pore clusters, completely isolated from each other (Figure 4.22 K, M). The largest two clusters (volumes > 10$^6$ voxels) accounted for 94% of the pore space in the subvolume and 13% of the analysed subvolume (Figure 4.22 K, Table 4.3). After 2455 hours of compaction, the pore space was accommodated mostly by two large clusters forming above and below the phyllosilicates layer, and together they constituted 88.5% of the pore space and only 7% of the subvolume (Figure 4.22 M, Table 4.3). The remaining porosity was accounted by smaller disconnected pores. The increasing number of disconnected pores (381 to 699) was consistent with a decrease in pore interconnectivity.

In the sample with glass beads and biotite, the pore space remained interconnected until 1205.5 hours of compaction where it started to become disconnected as seen in Figure 4.22 O. The largest pore cluster progressively decreased from 99.8% to 98.5% in these hours of compaction (Table 4.3). After 2465 hours of compaction, the pore space was disconnected in smaller clusters (Figure 4.22 P). The largest pore only accounted for 54.5% of the pore space at this stage, and 3.5% of the chosen subvolume (Table 4.3). From the 3D rendering another ten pore clusters larger than 10$^7$ µm$^3$ were present: these pore clusters, together with the largest one, accounted for 75.7% of the total pore space. As for the previous experiments, a decreased interconnectivity was emphasized by the increase number in disconnected
4.5 Results of digital image analysis

pores, which, across 2465 hours, is almost four times greater (from 228 to 1113).

The same analyses were performed on eroded data, and results visualised in three dimensions, to verify if the segmentation has some control on the interconnectivity (cfr. chapter 2, sections 2.5.3 and 2.5.3.4). The segmented pores have been eroded by one cubic voxel and label analysis was recalculated. In all cases, the interconnectivity did not change in eroded data, indicating that the degree of interconnectivity was bigger than a cubic voxel.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vertical shortening</th>
<th>Largest vs Tot. Pore space [%]</th>
<th>Largest pore vs Subvolume [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl (2446.5 hrs)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 %</td>
<td>99.9</td>
<td>31.6</td>
<td></td>
</tr>
<tr>
<td>18%</td>
<td>99.8</td>
<td>23.3</td>
<td></td>
</tr>
<tr>
<td>25%</td>
<td>97</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td>NaCl-biotite (444 hrs)</td>
<td>21%</td>
<td>99</td>
<td>35</td>
</tr>
<tr>
<td>29%</td>
<td>98.3</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>39%</td>
<td>89.3</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>NaCl-biotite (2455 hrs)</td>
<td>17%</td>
<td>99.8</td>
<td>26</td>
</tr>
<tr>
<td>28%</td>
<td>94</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>35%</td>
<td>88.5</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>NaCl-glass beads (437.5 hrs)</td>
<td>16%</td>
<td>99.8</td>
<td>29</td>
</tr>
<tr>
<td>26%</td>
<td>99.6</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>32%</td>
<td>98.7</td>
<td>15.2</td>
<td></td>
</tr>
<tr>
<td>NaCl-biotite-glass beads (2465 hrs)</td>
<td>14%</td>
<td>99.8</td>
<td>22</td>
</tr>
<tr>
<td>21%</td>
<td>98.5</td>
<td>15.3</td>
<td></td>
</tr>
<tr>
<td>26%</td>
<td>54.5</td>
<td>3.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3: Tabulation of pore connectivity for increasing strain and different sample composition in the analysed subvolume (400³ voxels). Tot. pore space refers to the total pore space included in the analysed subvolume. Grey box highlights the values for the pure NaCl experiments.
Figure 4.22: Evolution of the pore space with increasing compaction for different sample compositions: A, B, C) NaCl-glass beads (6.64 MPa); D, E, F) NaCl-biotite, first run (6.64 MPa); G, H, I) Pure NaCl (6.64 MPa); J, K, M) NaCl-biotite, second run (6.64 MPa); N, O, P) NaCl, glass beads and biotite (6.64 MPa).
4.5 Results of digital image analysis

4.5.4 Skeletonization of pore volumes

Skeletonization analyses were performed on the longest run of experiments, for different sample compositions and increasingly shortened datasets, using the *Auto-skeletonisation* operator in Avizo® v.9 with default parameters (cfr. chapter 2, sections 2.5.3 and 2.5.3.4).

4.5.4.1 NaCl-biotite

In this sample, the analyses were performed on a subvolume containing only the layer with phyllosilicates, following the same procedure described in section 4.5.2 for the biotite layer in the NaCl-biotite sample. In the first compaction, the pore space within the central portion was organised in 45 connected skeletons, one of which was composed by 4620 segments (Table 4.4). This skeleton therefore constituted a long and extensive interconnected pore body within the biotite layer (Table 4.4, Figure 4.23 A). On the contrary, in the most deformed sample, the number of interconnected skeletons increased to 183 (Table 4.4, Figure 4.23 B). However, as seen in Figure 4.23, these bodies were clearly isolated from each other and therefore did not allow fluid percolation within the central layer. These skeletons were composed by up to 14 segments each, testifying that the pore space progressively broke apart and became less connected with increasing deformation, therefore the number of segments for each pore body progressively decreased (Figure 4.24).

![Figure 4.23: 3D rendering of the skeletonised pore space within the biotite layer for the NaCl-biotite sample in second run: A) 17% vertical shortening (22.5 hours), B) 35% vertical shortening (2455 hours). In A, the largest skeleton occupies the entire subvolume. Colourmap representing the thickness of the segments connecting each skeleton: red colour highlights bigger pores.](image-url)
Figure 4.24: Graph representing the evolution of skeletons with increasing compaction for the NaCl-biotite sample. The graph represents the relation between the number of skeletons (e.g. elements) and the number of segments per skeleton. Vertical shortening as percentages.

4.5.4.2 NaCl-biotite-glass beads

The results of the skettonization analysis show that the pore space is significantly reduced and progressively disconnected for this sample. At 10 % vertical shortening, the medial axis of the pore space was represented by 36 skeletons, the largest of which accounted for 55 % of the pore space. In the most deformed sample, the pore space was composed of 423 skeletons, the largest one accounting for only 12 % of the pore space (Table 4.4). The progressive disruption of the pore space in skeletons and segments is visible in Figure 4.25. With increasing vertical shortening, the pore space is progressively represented by more skeletons, but with a lower number of segments per skeleton. However, there is a significantly higher number of segments per skeleton compared to the NaCl-biotite sample.
4.5 Results of digital image analysis

Figure 4.25: Evolution of skeletons in the pore space for the NaCl-GB-biotite sample with increasing compaction. A) 10 % vertical shortening (22.5 hours), B) 26% vertical shortening (2465 hours). Colourmap representing the thickness of the segments connecting each skeleton: red colour highlights bigger pores.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vertical shortening</th>
<th>N°skeletons</th>
<th>Largest skeleton vs Tot Pore space</th>
<th>Largest skeleton vs Subvolume [%]</th>
<th>Tot. Nºsegments in largest</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl-biotite (2455 hrs)</td>
<td>17%</td>
<td>45</td>
<td>52</td>
<td>12</td>
<td>4620</td>
</tr>
<tr>
<td></td>
<td>35 %</td>
<td>183</td>
<td>2</td>
<td>0.05</td>
<td>14</td>
</tr>
<tr>
<td>NaCl-biotite-glass beads (2465 hrs)</td>
<td>10 %</td>
<td>36</td>
<td>55</td>
<td>12</td>
<td>7664</td>
</tr>
<tr>
<td></td>
<td>26 %</td>
<td>423</td>
<td>21.5</td>
<td>1.4</td>
<td>1552</td>
</tr>
</tbody>
</table>

Table 4.4: Tabulation of skeletonization analyses for increasing strain and different sample composition in the analysed subvolume (400³ voxels). Tot. pore space refers to the total pore space included in the analysed subvolume.
Chapter 4. Pressure-solution processes

4.5.5 Strain analysis

Outputs of 3D-DIC (volumetric Digital Image Correlation) analyses were visualised as vertical microtomographic slices through the middle of the samples for increasingly shortened datasets (cfr. chapter 2, section 2.5.3.5). For the volumetric strain field, darker colours represent negative values, indicative of compressional field. Values of the 3D-DIC were then divided by the time steps to calculate mean strain rates (s⁻¹).

4.5.5.1 Pure NaCl

3D-DIC was conducted on the two pure NaCl samples loaded at 6.64 MPa. In the first experiment, 3D-DIC revealed high values for maximum shear strain and very low volumetric strains in the first compaction step (Table 4.5, Figure 4.26 A, Figure 4.27 A). With increasing strain (28 %), 3D-DIC did not reveal any substantial deformation, until the sample reached 31 % vertical shortening. In these time steps, 3D-DIC revealed pervasive maximum shear strains within the sample, but the volumetric strains values were higher compared to the first time step (Table 4.5).

The 3D-DIC outputs for the pure NaCl compacted for 2446.5 hours showed higher values of maximum shear strain and lower values for volumetric strain throughout the sample at the beginning of the experiment (Table 4.5, Figure 4.26 B, Figure 4.27 B). With increasing deformation, the strain values homogenized in the sample: higher values of maximum shear and negative values for volumetric strain were only present where grains indent each other. At the end of the experiment, maximum values ranged from 0.08 to 0.12 for maximum shear strains, and from -0.15 to -0.05 for volumetric strains (Table 4.5).

Mean strain rates were also determined from the same datasets, for both runs. In the first run, mean strain rates decreased by an order of magnitude across the increasingly shortened datasets (Table 4.5, Figure 4.28 A, Figure 4.29 A). In the second run, strain rates decreased by two orders of magnitude over 2446.5 hours of compaction (Table 4.5, Figure 4.28 B, Figure 4.29 B).
4.5 Results of digital image analysis

Figure 4.26: The figures show maximum shear strain outputs, for different samples and increasing vertical shortening. Colour bar is the same for all figures and the image width equals the sample diameter, 5 mm.
Figure 4.27: The figures show the volumetric strain outputs, for different samples and increasing vertical shortening. Colour bar is the same for all figures and the image width equals the sample diameter, 5 mm.
4.5 Results of digital image analysis

4.5.5.2 NaCl-biotite

3D-DIC results for the first experiment after 24% vertical shortening showed higher values of maximum shear strain and negative values for volumetric strain where the phyllosilicates were located (Table 4.5, Figure 4.26 C, Figure 4.27 C). With increasing deformation, the sample showed still high values of maximum shear strain throughout the volume, indicating a stronger degrees of deformation: high values ranged from 0.06 to 0.15. Comparison with µCT data related these high values to grains indenting each other. After 444 hours of compaction, 3D-DIC revealed strong maximum shear values (ranging from 0.07 to 0.14) and very negative volumetric strain values (ranging from -0.10 to -0.05), in particular in the central biotite layer (Table 4.5).

Maximum shear strain rates remained close to $10^{-6} \text{ s}^{-1}$ for all increasingly shortened datasets, over 444 hours of compaction (Table 4.5, Figure 4.28 C). Volumetric strain rates decreased by an order of magnitude (Table 4.5, Figure 4.29 C). In the second experiment, DIC results still highlighted substantial deformation within the biotite layer (Figure 4.26 D, Figure 4.27 D). With increasing strain, strain values homogenized; however, 3D-DIC still showed pronounced values within the biotite layer. High maximum shear values range from 0.04 to 0.06, while negative values of volumetric strain range from -0.04 to -0.08, and they are much lower compared to the previous correlation step (Table 4.5, Figure 4.26 and Figure 4.27). Between these two time steps, strain rates decreased by an order of magnitude (Figure 4.28). Maximum shear and volumetric strain values were substantially higher at 32% vertical shortening after 1208 hours of compaction, and at the end of the experiment too. In these time steps, the central biotite layer was characterised by very negative compresional values (-0.16 to -0.05) and very high maximum shear strain values, ranging from 0.09 to 0.26. Mean maximum strain rates indicated high values of $7 \times 10^{-8} \text{ s}^{-1}$ (Figure 4.28 D). The lowest rates for volumetric strain reached $-7 \times 10^{-8} \text{ s}^{-1}$ at the end of the experiment (Table 4.5, Figure 4.29 D).

4.5.5.3 NaCl-glass beads

3D-DIC outputs are much different in the presence of glass beads (Figure 4.26 E, Figure 4.27 E). Comparisons with µCT data show that most deformation highlighted by the 3D-DIC results was accommodated by the glass beads: high values of maximum shear strain (ranging from 0.16 to 0.32) and high volumetric strains (from 0.27 to 0.88) are located either within or surrounding the glass beads. With increasing strain, the strains decreased; however, they still remained high in the neighbourhood of the beads. Mean shear strain rates approximated $4 \times 10^{-6} \text{ s}^{-1}$ of magnitude in the first 22.5 hours of compaction after 21% vertical shortening, but they progressively
Chapter 4. Pressure-solution processes

decreased to $4 \times 10^{-7} \text{s}^{-1}$ after 444 hours of compaction (32% vertical shortening) (Table 4.5, Figure 4.28 E). The lowest volumetric strain rates decreased by an order of magnitude (Table 4.5, Figure 4.29 E).

4.5.5.4 NaCl-glass beads-biotite

In this sample, glass beads seemed to accommodate most of the deformation, as for the NaCl and glass beads sample. However, comparison with µCT data revealed that extremely high values were localised where the phyllosilicates were present: in these areas, maximum strain values ranged from 0.09 to 0.17 (Figure 4.26 F), and volumetric strains from -0.03 to -0.15 in compressional fields (Figure 4.27 F, Table 4.5). Glass beads on the contrary were highlighted by high maximum shear strains but also very positive volumetric strains (e.g. dilatation field). Negative values were however also present surrounding glass beads (from -0.30 to -0.45).

Overall, the sample showed mean maximum shear strain rates lower than $1.7 \times 10^{-6} \text{s}^{-1}$ in the first few hours of compaction (14% vertical shortening) (Table 4.5, Figure 4.28 F). With increasing deformation, the rates decreased by two orders of magnitude, as well as volumetric strain rates (Table 4.5, Figure 4.29 F).
4.5 Results of digital image analysis

Figure 4.28: Strain rates ($s^{-1}$) for the maximum shear strains calculated from 3D-DIC outputs for different samples and increasing vertical shortening (in percentages). Image width equals the sample diameter, 5 mm.
Figure 4.29: Strain rates (s\(^{-1}\)) for the volumetric strains calculated from 3D-DIC outputs for different samples and increasing vertical shortening (in percentages). Image width equals the sample diameter, 5 mm.
### Table 4.5: Tabulation of 3D-DIC results for increasing strain and different sample composition. Strain rates in [s$^{-1}$].

<table>
<thead>
<tr>
<th>Sample Composition</th>
<th>ε$^s$ (highest)</th>
<th>ε$^v$ (lowest)</th>
<th>ε$^y$ (highest)</th>
<th>ε$^v$ (lowest)</th>
<th>ε$^s$</th>
<th>ε$^v$</th>
<th>ε (highest)</th>
<th>ε (lowest)</th>
<th>Vertical Shortening [%]</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl (227.5 hrs)</td>
<td>170.07</td>
<td>-0.21</td>
<td>-0.22</td>
<td>-0.07</td>
<td>5 x 10$^{-6}$</td>
<td>-4 x 10$^{-6}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl (310.07</td>
<td>100.07</td>
<td>-0.12</td>
<td>-0.11</td>
<td>-0.03</td>
<td>6 x 10$^{-7}$</td>
<td>-8 x 10$^{-7}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl-biotite (444 hrs)</td>
<td>240.06</td>
<td>-0.12</td>
<td>-0.14</td>
<td>-0.08</td>
<td>1.7 x 10$^{-6}$</td>
<td>-3 x 10$^{-6}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl-glass beads (437.5 hrs)</td>
<td>160.16</td>
<td>-0.32</td>
<td>-0.17</td>
<td>-0.08</td>
<td>4 x 10$^{-6}$</td>
<td>-5 x 10$^{-6}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl-biotite-glass beads (2455 hrs)</td>
<td>140.09</td>
<td>-0.17</td>
<td>-0.15</td>
<td>-0.03</td>
<td>3.4 x 10$^{-6}$</td>
<td>-5 x 10$^{-6}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: All values are rounded to the nearest significant figure.
4.5.6 Microstructural analysis

SEM images of the recovered samples of the last CT experiment were obtained using secondary electron imaging (cfr. chapter 2, 2.5.1.6).

4.5.6.1 Pure NaCl

The sample showed indentations of NaCl grains and in some parts it was possible to recognize triple junctions and grains losing their cubic habit. Suture zones were present at grain interfaces, where the two grain boundaries highly indented each other (Figure 4.30 B, C).

4.5.6.2 NaCl-biotite

Where phyllosilicates were present: i) grains became highly indented ii) NaCl grains indented biotite flakes, iii) grains lost their cubic habit and became more rounded (Figure 4.30 D, E). Where phyllosilicates were absent, indentations between NaCl-NaCl grains still occurred, showing triple junctions, but grains retained more of their original cubic shapes, and more porosity was present, as seen from the µCT data.

4.5.6.3 NaCl-biotite-glass beads

In this sample, glass beads visibly indented NaCl grains, which developed a curved grain boundary due to the compaction (Figure 4.30 F). High degrees of indentations were also visible at NaCl-biotite interfaces. At higher magnifications, it was possible to recognize dissolution features at the glass-NaCl interface, and possibly newly precipitated material: as the samples were recovered from the vessels when they were saturated with NaCl solutions, it was not possible to establish with absolute confidence whether this was newly precipitated material or crystallised NaCl from evaporation of residual solution.
4.5 Results of digital image analysis

Figure 4.30: Secondary electron images of recovered samples. A) Undeformed sample of pure NaCl. Shadows are given by the high charging of the sample. B) pure NaCl; C) close up of pure NaCl sample; note the suture zone. D) NaCl-biotite sample; E) NaCl-biotite sample; F) NaCl-biotite-glass beads sample; with close up on indentations of glass beads.
4.6 Discussion

4.6.1 Mechanical and chemical processes during uniaxial compaction

The compaction curves for all performed experiments resemble published experimental curves for various rock-analogue materials. However, the duration of the longest compaction experiments considerably exceed those of many published studies (Spiers et al., 1990; Rutter and Wanten, 2000; Renard et al., 2004; Zhang and Spiers, 2005; Zhang et al., 2010). The compaction curves show a gradual change in the gradient, which decreases in steepness from the first hours of compaction towards the end (Figure 4.5 A, Figure 4.9 A, Figure 4.11 A).

To discriminate the effect of initial packing of grains on the final vertical shortening of the samples, the latter was also calculated by taking as starting point the time step relative to the first 20 hours of loading (Figure 4.5 B, Figure 4.9 B, Figure 4.11 B). These figures showed that:

- The presence of biotite in the sample induces a greater vertical shortening compared to pure NaCl sample (∼4%) (Figure 4.9 B);
- NaCl-glass-biotite sample compacts more compared to the pure NaCl samples, and less compared to the NaCl-biotite samples, as expected;
- All compaction curves show a gradual increase in the gradient with time, which indicates that compaction is still ongoing. This is particularly important for the longest run, where PSC processes dominate the deformation, and especially for the NaCl-biotite sample, as it reflects strain partitioning in the sample (cfr. Figure 4.13, sections 4.5.1.3 and 4.6.3).

The overall change in gradient present in the compaction curves reflects a transition between two end-members due to a change in the kinetics, from physical to chemical. The data in fact can be fitted through a power law equation in which \( \dot{\varepsilon} \) is proportional to \( t^n \), where \( n \) defines the slope of the power law fit (Renard et al., 2001). However, in these data, where the slope is changing with time, the total amount of strain rate is given by two power law equations with different exponent \( n: \dot{\varepsilon}_{tot} = \dot{\varepsilon}_1 + \dot{\varepsilon}_2 \), where \( \dot{\varepsilon}_1 \sim t^{n_1} \) and \( \dot{\varepsilon}_2 \sim t^{n_2} \) (Figure 4.31). The results indicate that the exponents of the power law equations range from 1.25 to 1.4 for \( n_1 \), and from 0.17 to 0.3 for \( n_2 \) (Figure 4.31).

In the datasets corresponding to the change in gradient, 3D-DIC results do not show strong values, and the samples appears almost homogenized. In some cases, 3D-
DIC did not correlate these datasets. While 3D-DIC can clearly help to discriminate between physical and chemical processes, in combination with an accurate visual inspection of the µCT data, it is unclear why 3D-DIC did not work on the datasets corresponding in the change of gradient. However, the homogenization in strain values can represent a change in the kinetics of the system, as strain values are expected to lower as the change from mechanical to chemical processes occur. This is testified by the decreasing slopes of the best fit curves. Following this reasoning, the total amount of deformation can be divided in two domains, characterised by different strain rates and kinetics, which reflect the relative contributions of different end-members processes (Figure 4.31). The first domain, with a slope ranging from 1.25 to 1.4, is dominated by physico-mechanical processes (i.e. grain sliding, grain re-arrangement) and it is characterised by higher strain rates occur. The vertical microtomographic slices of the respective time steps showed a reduction of the pore space and grain re-arrangement. No microfracturing or grain fragmentation was observed in the performed experiments. This is consistent with studies conducted by Schutjens and Spiers (1999) and Marmottant et al. (2008), which indicate that microfracturing in NaCl is unlikely to be observable at stresses below 28 MPa, a threshold substantially higher than the one used in the present study. The second part of the curve is typified by lower strain rates, and the samples compact more slowly. A visual inspection of the respective µCT data showed that grains progressively indent, and porosity is decreased (∼20-30%) (Figure 4.32, cfr. section 4.5.1). This second domain, typified by a lower slope (ranging from 0.17 to 0.3), is dominated by chemical processes. In this second domain, pressure-solution processes are active. However, some contribution might derive also from Ostwald ripening processes (Baldan, 2002; Oliva-Ramirez et al., 2016). During this process, small particles dissolve and reprecipitate onto larger particles, resulting in an equal average grain size. This can be particularly true in the case of phyllosilicates, in which grains are glued together over time as a result of either pressure-solution acting alone, or together with Ostwald ripening processes.

The strain rates measured with 3D-DIC are higher than the ones present in nature, by a few orders of magnitude, because of the intrinsic nature of NaCl to accelerate the process (Gratier, 1993; Gratier et al., 2013). The strain rates measured here are on the same order of magnitude as the studies reported by Spiers et al. (1990) and Renard et al. (2001). Nevertheless, in the presence of phyllosilicates, 3D-DIC highlighted very strong maximum shear strains and very low (compressional) volumetric strain values. Calculations of the relative strain rates indicate that the presence of phyllosilicates contributes to increasing the maximum shear rates and to lowering the volumetric strain rates of the process compared to the NaCl layers.
Chapter 4. Pressure-solution processes

and samples. The same behaviour is observed in the case of glass beads, although, as discussed in section 4.6.4, this might be related to the movement of glass beads between the different compaction steps.

![Graph showing compaction curves with best-fits](image)

**Figure 4.31:** Best-fits of the longest compaction curves. The best-fits were calculated through power-law equations, with exponents $n_1 = 0.17-0.3$ and $n_2 = 1.25-1.4$. The change in exponent, and therefore slope, marks a change between two domains, dominated by different processes. A first domain, physico-mechanical, is characterised by grain rearrangement and/or grain sliding. The second domain is dominated by chemical processes, which include pressure-solution and potentially Otswald ripening.

### 4.6.1.1 Effect of uniaxial load

In all experiments, the samples loaded at greater uniaxial load (6.64 MPa) experienced more compaction than the samples loaded at 1.66 MPa (Figure 4.5 B, Figure 4.11 B). From the vertical µCT slices, it is possible to recognize that the samples loaded at 1.66 MPa show a considerable amount of porosity left at the end of the experiments (~ 30% in contrast to ~ 40% in the case of pure NaCl sample), compared to the same sample compositions loaded at 6.64 MPa. From Equation 4.1 (see section 4.2.1), it follows that a lower applied uniaxial stress will induce a lower strain rate on the process, therefore resulting in lower porosity reduction and fewer grain indentations. However, this can be overcome by increasing the temperature to accelerate reaction kinetics (Rutter, 1983).
4.6 Discussion

Figure 4.32: Vertical µCT slices showing the evolution of the NaCl-GB-biotite sample over time. Note the progressive reduction of pore space between grains.

4.6.2 Pressure-solution in pure NaCl samples

Overall, in the pure NaCl samples, PSC affects the bulk porosity and pore sizes distribution with time, but it does not affect the pore connectivity nor induces very high maximum shear and volumetric strains.

Comparison between 3D-DIC outputs and vertical µCT slices highlighted that high maximum shear strains and negative volumetric strains in the first compaction hours are related to grain re-arrangement and porosity reduction, while in the time steps relative to the second part of the compaction curve 3D-DIC highlighted grain indentation areas, caused by an initial stage of PSC. However, these strain values are low compared to the NaCl-biotite samples (from 0.08 to 0.10 for maximum shear strain), and they do not increase with deformation (Figure 4.26 A, Figure 4.26 B, Figure 4.27 A and Figure 4.27 B). The outputs do not show any significant strain localisation, compared to the samples compacted in the presence of phyllosilicates.
SEM imaging showed the presence of suture zones between NaCl grains: these suture zones also showed dissolution features, similar to those reported by Urai et al. (1986) and Schenk et al. (2006).

4.6.3 Pressure-solution in the presence of phyllosilicates (e.g. biotite)

The experimental samples mixed with biotite show a significant vertical shortening and reduction in pore space and connectivity over time. Particularly, there is a substantial difference in the evolution of porosity between the central biotite layer, and the marginal NaCl layers. Where phyllosilicates are present, local porosity decreases approaching 0% (see section 4.5.1.3). The pore space becomes highly disconnected, and hydraulic compartmentalisation occurs (Figure 4.22 D-F, and J-M, see section 4.5.4 and Figure 4.23). This is reflected in the pore size evolution, which shows a ~90 % decrease in big pore sizes compared to the pure NaCl marginal layers (~50 %) (Table 4.2, Figure 4.18 A, B). Porosity and deformation were partitioned differently into these layers (Figure 4.13 C, D). While in the pure NaCl sample, strain is linearly accommodated over time, measurements of the thickness of the central and marginal layers of the NaCl-biotite sample indicated that in these layers the vertical shortening is non-linear, reflecting a partition of the process into the two layers (Figure 4.13 D).

These results confirm that the presence of phyllosilicates enhances the rate of PSC and induces a ~100% reduction of porosity (see section 4.5.1) and higher degrees of grain indentations compared to pure NaCl (Figure 4.10, Figure 4.30). A phyllosilicate layer, existing as a heterogeneity, can be a precursor which promotes pressure-solution process, affecting the evolution of porosity in the rocks and reducing pore connectivity, thereby promoting the formation of stylolites. In this sense, the localisation of the pressure-solution process observed in the described experiments can be interpreted as the initial stage of a stylolite formed synthetically. From these results, it follows that the presence of phyllosilicates might act as natural barrier to any vertical fluid flow, while potentially promoting flow parallel in the marginal NaCl layers, where bulk porosity still remains present and highly interconnected, therefore allowing permeability and fluid percolation (Heap et al., 2014).

4.6.3.1 How does PSC occur in the presence of phyllosilicates?

PSC between NaCl and biotite can be modelled following the theoretical equations of Aharonov and Katsman (2009), in which dissolution and re-precipitation of material between the water film and the adjacent pores is driven by a chemical potential...
dissolution. It can be inferred that at the beginning of the pressure-solution process, enhanced chemically diffuse dissolution occurs and transport distances are limited to the scale of several grain diameters (e.g. within the biotite layer), where the difference in chemical potential is higher, as highlighted by the 3D-DIC outputs (Figure 4.33-1, 2) (Bjørkum et al., 1998; Aharonov and Katsman, 2009). With increasing deformation, the porosity is critically reduced and the pore connectivity breaks down in the biotite layer, causing the saturated solution to remain trapped within the biotite layer where the processes become less effective. With increasing deformation, the uniaxial load is distributed over the increasingly flatter surfaces of the biotite layer, and contact areas increase, therefore lowering the stress load. This causes the chemical potential difference to decrease and therefore the active dissolution front to migrate towards the marginal NaCl layers, where pore space and pore connectivity allow transportation of ions in solution. The active dissolution fronts are now established at the interfaces between pure NaCl and NaCl-biotite domains, towards the marginal layers, where the difference in chemical potential is higher (Figure 4.33-3). This is furthermore confirmed by the 3D-DIC outputs, which showed a diffused area of increased deformation surrounding the biotite layer in the most deformed datasets (Figure 4.26 D). Precipitation of NaCl, by transport controlled surface reactions (Bjørkum et al., 1998), occurs in the marginal NaCl layers (Figure 4.33-4).
Figure 4.33: Schematic model for stylolite formation: 1) Starting condition: biotite pre-localised but not pre-aligned within a NaCl material (e.g. sandstone) 2) After some compaction, the active dissolution front origins at the interface between pure NaCl layers and biotite grains. Porosity starts to reduce. 3) Precipitation occurs, by transport controlled surface reactions, within the biotite layer. Biotite grains start to align and porosity is reduced. 4) With increasing deformation, porosity is critically reduced in the biotite layers, and transport distances move towards the marginal NaCl layers, where active dissolution occurs at the interfaces between NaCl and biotite, and new precipitation sites form within the NaCl layers. On the left, a schematic relative contribution to compaction, mechanical and chemical, in the two layers is reported. A relative contribution to precipitation is also presented.
4.6 Discussion

4.6.4 Pressure-solution in the presence of glass beads

Glass beads (0.5 mm diameter) were mixed with sieved NaCl and NaCl-biotite samples to monitor the evolution of the pressure-solution process in the presence of a harder structural heterogeneity. Glass beads were chosen because of the rounded shape, which makes this material easily recognizable. The presence of glass beads has a substantially different effect on the evolution of porosity and pore connectivity during ongoing pressure-solution compared to pure NaCl and NaCl-biotite sample. Both samples, NaCl-glass beads and NaCl mixed with biotite and glass beads, show a smaller decrease in pore connectivity compared to the NaCl-biotite samples with increasing compaction (Figure 4.22 A-C and N-P). In particular, in the NaCl-glass beads sample, pore connectivity is maintained, showing only a minor reduction of the pore space (Figure 4.22 A, B, C). With increasing deformation, smaller pores are created, indicating that deformation strongly cut off larger pores (Table 4.2).

The comparison between µCT data and volumetric 3D-DIC shows high degrees of grain indentations at the interfaces between the glass beads and NaCl grains, in the most deformed sample (Figure 4.12 B). In this dataset, 3D-DIC shows very high maximum shear strains within or surrounding the glass beads (Figure 4.26 E): these values represent a more diffused but still localised pressure-solution process, where the localisation occurs at the interfaces between the glass and NaCl grains. The positive values shown by the volumetric strains in the 3D-DIC are interpreted as to be the results of glass beads movement and therefore not indicating a real dilatational field. The movement of glass beads may have introduced more "deformation" in the samples than the actual process: when two datasets are compared, the code only picked up the relative movement of glass beads and NaCl grains, and not the actual grain indentations or any force chain that might have been present. Higher maximum shear strains in the less deformed datasets are interpreted as the results of grains sliding past each other and grain rearrangement: comparison with the µCT data confirmed that these values are associated with pore spaces, therefore indicating that, in the first compaction datasets, pore space reorganised due to the mechanical grain rearrangement, and no microfracturing has been observed (cfr. section 4.6.3). The 3D-DIC results are similar to those reported for the NaCl-glass beads-biotite sample, although substantially higher maximum shear strain values and lower volumetric strain values are present where the phyllosilicates are located, thus partially resembling what happened in the NaCl-biotite (Figure 4.26 F, Figure 4.27 F). The same trends are observed along the compaction history, as for the NaCl-biotite and NaCl-glass beads samples.

The presence of glass beads within a granular media acts as more competent
structural heterogeneity, localising the pressure-solution process at interfaces between NaCl and glass beads and where the difference in chemical potential is higher. Furthermore, the localisation of the pressure solution along NaCl-glass beads interface, but with porosity still present, may represent an initial stage in the development of force chains. A force chain is a "heterogeneous distribution of interparticle forces" (Bassett et al., 2015) and they represent a chains of particles where the stresses are higher than the average (Peters et al., 2005; Bassett et al., 2015) and where grains transfer forces to each other. The beads act as a harder structural heterogeneity inducing a much higher stress on the surrounding NaCl grains, which indent other grains, creating a force chain.

4.6.5 Pressure-solution in the presence of glass beads and biotite

The same overall trend of NaCl-glass samples is observed in the NaCl-biotite-glass beads sample. However, the presence of phyllosilicates clearly affected the evolution of porosity, grain arrangement and pore connectivity with increasing compaction. Pore connectivity is significantly reduced with increasing compaction, breaking the pore space into smaller disconnected clusters (Figure 4.22 P). There is no clear indication of strain localisation as it occurred in the NaCl-biotite sample. Skeletonisation analyses revealed that, with increasing compaction, the pore space progressively disconnects, forming more isolated skeletons, made up of several branches (see section 4.5.4, Figure 4.25). However, this decrease in connectivity is less pronounced than in the NaCl-biotite sample and it does not appear to be directional, but rather uniformly distributed. Phyllosilicates progressively wrapped around the beads, at the highest level of strain, forming strain caps (Figure 4.34). From Figure 4.34 B, strain caps are already forming after 19 % vertical shortening, which corresponds to 136.5 hours of compaction, quite early in the compaction history. It might be interpreted that the areas of breaking connectivity are related with the presence of biotite flakes.

The presence of glass beads and biotite in NaCl sample resembles many natural geological scenarios, where a harder competent material is in contact with some clays (e.g. sandstone with clays and abundant quartz enrichment or carbonate sand). Pressure-solution in quartz, quartz arenites/sandstone and carbonate sands has been modelled and analysed over a number of studies (Boer et al., 1977; Angevine and Turcotte, 1983; Cox and Paterson, 1991; Gratz, 1991; Mollema and Antonellini, 1996; Bjørkum et al., 1998; Rutter and Wanten, 2000; Niemeijer and Spiers, 2002; Croizé et al., 2010). In Boer et al. (1977) and Angevine and Turcotte (1983), results indicated that dissolution occurred within grain contact areas, and the dissolved
4.6 Discussion

material precipitated within the pore space on adjacent grains, leading to destruction of primary porosity (Figure 4.35 A, B). Similarly, experimental results indicate that dissolution occurred on grain contact areas, and transport distances may be limited to adjacent grains. Following this interpretation, it can be argued that pore shape changes were not identified because, as compaction proceeds, precipitation of new material occurs on lower stressed areas, therefore the overall shape of the pore is maintained, but it reduces in volume with time (cfr. 4.6.6).

The progressive reduction in pore connectivity with deformation has important implication for fluid percolation as it introduces a hydraulic compartmentalisation in the rock. This induces the development of new fluid pathways, which can critically modify the rock. This must be considered carefully when modelling fluid flow and PSC in quartzose arenites or sandstones, in which phyllosilicates, or more generally clays, might be present.

Figure 4.34: 3D renderings of a subvolume from the sample NaCl-glass beads-biotite, showing the progressive evolution of the pore space (red) and biotite flakes (green) around the glass beads (light blue) for increasingly shortened datasets: A) 10 %, B) 19 %, C) 26 %. 3D rendering of the spatial evolution of biotite flakes around the glass beads with increasing compaction: D) 10 %, E) 19 % and F) 26 %.
4.6.6 Precipitation sites: overgrowth or neo-nucleation?

Despite pressure-solution processes have been deeply studied over the last decades, the current knowledge lacks of data on the precipitation mechanisms of the dissolved material. Visual inspection of the microtomographic datasets could not determine where precipitation occurred, nor whether the precipitated material is the result of overgrowth or neo-nucleation mechanisms. Moreover, SEM microstructural analyses of the recovered samples did not allow to establish with absolute confidence whether there was newly precipitated material or crystallised NaCl from evaporation of residual solution (cfr. 4.5.6). Despite this, microstructural images indicate crystallization of some newly formed NaCl grains (Figure 4.36 A, B, C) These grains have dimensions of few tens of microns (20-30 µm), and they are characterised by a rounded shape. They are present on the surfaces of beads or NaCl grains, and they overgrow old NaCl grains. Glass beads also show on their surfaces inhomogeneous crystallization of NaCl: these crystallizations are more random and less crystalline than the previous described microstructures, and considerably smaller (< 10 µm) (Figure 4.36 D). For these reasons, I infer the first microstructures to represent precipitated NaCl from PSC, and therefore testifying, at least in the case of a harder structural heterogeneity, that transport distances are limited to adjacent
4.6 Discussion

grains. The precipitation occurred as a combination of neo-nucleation and overgrowth processes. On the contrary, the second type of microstructures represent crystallised NaCl from evaporation of residual solution. Additional information on the location of precipitation sites could derive from fluorescence analyses, which would allow identification of the precipitation fronts.

![BSE images in secondary electrons showing possible precipitation sites. A) Newly formed NaCl grains on the surfaces of glass beads. B-C) Close ups of the newly formed NaCl grains on the surfaces of the beads. D) Close up of crystallised NaCl from evaporation of residual solution.](image)

4.6.7 Effects of segmentation/separation algorithms

Bulk porosity and pore size, shape and orientation analyses can be influenced by the chosen separation/segmentation method, especially when the threshold value is chosen manually (Leu et al., 2014). However, these analyses were visually inspected and carefully assessed to choose the best threshold values and introduce minimum errors. The precision of the threshold value was checked by overlaying the segmented slices to the grey-scale reconstructed images, in two dimensions and three dimensions (cfr. chapter 2, section 2.27). This allowed adjustment of the chosen values with respect to the original data.
Furthermore, error bars on bulk porosity analyses and pore connectivity were obtained by morphologically eroding and dilating the segmented data by one voxel (cfr. chapter 2, sections 2.4.3 and 2.5.3). In isotropic clusters, the morphological erosion/dilation retain the shape and orientation of the original clusters; however, it provides the largest possible errors of the segmented volume fraction, which, in this way, are exaggerated (Liu and Regenauer-Lieb, 2011; Fusseis et al., 2012). The error bars in Figure 4.16 show a progressive decrease, accordingly to the reduction in bulk porosity. This is expected since the original volumes are decreasing, hence the upper and lower bar are decreasing accordingly. However, in some cases (NaCl-biotite and NaCl-GB-biotite samples) the upper and lower limit of the error bars are not the same. In both cases, the upper bar, given by the dilation, is greater than the lower bar. This is interpreted as a direct effect of the dilation operation: dilating the data by one voxel is sufficient to include in the calculation pore throats that were otherwise discarded from the analysis. It is recognised that, although this operation does not induce shape changes, it does influence pore structures, as pores connected by narrow pore throats can become easily disconnected due to a morphological erosion, or become connected in the case of a dilation (similarly to what described in chapter 3, section 2.4.3). Nevertheless, the calculated error bars mirrored the evolution of porosity with increasing strain. These observations, combined with the measurement of bulk porosity by mass weight (cfr. 4.5.1), prove that the adopted workflow is consistent, and it overestimates errors introduced by the segmentation algorithms.

As Ji et al. (2012) reported, another potential source of errors is given by the filtering algorithm. The study found that the bigger the kernel size, the more the results change (e.g. percentage in macroporosity), introducing substantial miscalculations in the data. However, the kernel size chosen here is relatively small compared to that study (e.g. two vs five), therefore any potential error is considerably reduced in these experiments. Avizo®’s separation algorithm can also introduce errors (see chapter 2, section 2.5.2.4 and 2.26). I conducted some tests in which I changed the parameters of the separation (from marker one to two, cfr. chapter 2, section 2.5.2.4). The results suggest substantial differences in both shape and orientation analyses, thus indicating that the outcome of the analyses are subject to the method of separation applied. However, as Ji et al. (2012) suggested, an optimal way of minimizing errors is to choose a consistent workflow between undeformed and increasingly deformed datasets: in all studied datasets, the chosen workflow was applied consistently, to provide useful insights into macro-connectivity and porosity evolution with increasing deformation.
4.6 Discussion

4.6.7.1 Cropping

Another potential source of errors is created by the clipping plane and cropping operator. Pores laying on the edges may in fact show shape and orientation artefacts which have been introduced with the cropping action. The Avizo® operator called Border kill can be used to exclude from the analyses objects intersecting the edges and influenced by the clipping plane. New analyses on the sample NaCl-biotite were conducted on the new labelled data (see Appendix C, Figure C.3). The results show no substantial change for shape and orientation analyses from the non-filtered data: the only substantial effect is visible in the pore size distribution, as, in the highest degree of compaction, big pores, which are laying on the edges, are discarded from the analyses. Therefore, for all the analyses conducted, I have assumed that these artefacts are not sufficient to influence the outcome of my interpretation of the data.

4.6.8 Effects of size lower threshold at 10 or 125 cubic voxels

Pore size distributions for the experiments have also been plotted for sizes larger than 125 cubic voxels instead of 10 (Figure 4.37). The curves show few differences compared to size distributions with a lower threshold at 10 cubic voxels (Figure 4.17). However, few intermediate sizes (10^4-10^5 µm^3) are eliminated from the analyses, potentially missing important information about porosity evolution (Table 4.2). Hence the choice of a lower threshold at 10 voxels for the pore size distribution analyses. The overall trends are nevertheless maintained across increasingly shortened datasets.
4.7 Summary

In this study, I have combined computed X-ray microtomography with volumetric DIC and SEM imaging to monitor the spatio-temporal evolution of the pressure-solution process, and its effect on bulk and local porosity, pore connectivity, grain morphologies and fluid percolation. Computed X-ray microtomography allows measurements of the vertical shortening of the samples from the vertical µCT slices for each compacted dataset, and therefore the creation of compaction curves. Analysis of the compaction curves, and comparison with the relative vertical µCT slices, identified that compaction curves are characterised by a gradual change in gradient. At the beginning of the compaction, the curve is characterised by a very steep gradient. Visualisation of the respective microtomographic data indicate that grain packing and rearrangement are present: no microfracturing or fragmentation was observed from the visual inspection of the respective µCT datasets. The second part of the curve is dominated by a more gradual gradient: visual inspection of the respective µCT datasets confirms that grains exhibit higher degrees of indentations, and there is a reduction of bulk porosity and pore connectivity, indicating that PSC processes are active. Overall, the compaction curves show that uniaxial compaction still occurs at the end of the experiments, at slower rates, even in the longest runs.

The combination between µCT data and volumetric DIC allowed calculation of the strain values, from which the mean rates throughout the experiments can also be calculated. For all experiments, maximum shear and volumetric strain values were more pronounced in the first hours of compaction, and in the second part of the compaction curve. Higher strain rates are found where phyllosilicates were present, confirming that their presence accelerated the process, as shown previously by Hickman and Evans (1995), Bos et al. (2000a), Bos and Spiers (2000), and Aharonov and Katsman (2009). In the presence of phyllosilicates, pore connectivity was strongly reduced, and fluid pathways were significantly modified.

Fluid percolation was substantially impeded vertically with increasing compaction, as indicated by the pore skeleton analyses. In this sense, the phyllosilicate layer may represent a barrier for vertical fluid flow; however, fluid flow can be promoted in the marginal layers, where porosity and connectivity are maintained even at the highest degree of deformation, similarly to the conclusion of Heap et al. (2014).

The presence of glass beads and phyllosilicates in NaCl mixtures created disconnected porosity in the sample. The number of disconnected pores was substantially smaller than in the NaCl-biotite samples, however, it might be inferred that the areas of breaking connectivity are related with the presence of biotite.
flakes. This heterogeneous pore space creates preferential pathways for fluid infiltration. Phyllosilicates progressively wrapped around the beads with increasing compaction, forming strain caps, localising pressure-solution processes and causing a drastic reduction in pore space and pore connectivity (Figure 4.22 N, O, P). Where phyllosilicates are not present, the beads indent NaCl grains, triggering higher stresses on the grains and forming a similar outcome to force chains.

Following these observations, it is evident that the kinetics and thermodynamics of the pressure-solution processes are much more complicated and heterogeneous than previously thought. The combination of µCT with 3D-DIC and SEM imaging provided a multi-dimensional characterization of the process offering new insights.
Final remarks
5.1 Final discussions

5.1.1 Advances in fluid-rock interaction: what can µCT add to current investigation?

The combination of µCT with 2D analytical techniques provided new insights into the 4D evolution of porosity and reaction microfabrics during fluid-rock interaction. The analyses of the reaction microfabrics in the Kråkeneset gabbros allowed the identification of garnet deformation mechanisms, and spatial distribution of fluid infiltration around deforming phases. It highlighted the potential of µCT in visualising microfabrics in 3D and obtaining qualitative and quantitative data used in determining the geological history of the rock. These analyses also raised new questions on garnet rheology, 3D arrangement of reaction microfabrics, and extent of the fluid infiltration.

Despite garnet has being described to deform by dislocation creep at these metamorphic conditions (Ji and Martignole, 1994, 1996), no evidence for crystal plasticity was found. These results are coherent with experimental studies which confirmed the absence of intracrystalline dislocation creep at similar metamorphic conditions, in response to the presence of water in the system, which significantly reduced the mechanical strength of garnets (Voegelé et al., 1998; Wang and Ji, 1999; Zhang and Green, 2007). This finding expands the current knowledge of garnet rheological behaviour during fluid-rock interaction and shear localisation mechanism.

Reaction microfabrics are conventionally investigated in 2D to obtain information on the P-T-t path of the rock, deformation mechanisms, element transport, and fluid flow. However, missing information on the third dimension can strongly bias the final interpretations, as shown in chapter 3. The open structures of garnet coronas leave space for element transport to and from olivine grains, affecting the reaction propagation front, because elements are free to be transported elsewhere in the sample. These observations are similar to those reported by Hughes et al. (2016), who demonstrated that symplectites reaction textures do not form around individual grains, but rather form an open network which preserves evidence of fossil fluid pathways. The garnet coronas in Kråkeneset are also connected to each other, potentially forming a load-bearing framework within the rock. Moreover, the cluster size distribution of the intermediate strain domain and respective 3D visualisation revealed the presence of small cloudy patches of garnets. I infer the 3D spatial arrangement of these garnets to be related to synkinematic fluid infiltration, and can therefore be used to trace fossilised fluid pathways. With increasing strain,
garnets are progressively rearranged in oblate clusters. This spatial rearrangement was accommodated by microfracturing and passive granular flow, with ongoing nucleation and overgrowth of former garnets while the rock was deforming. The new spatial distribution into elongated clusters may act as preferential fluid pathway, redirecting fluid flow parallel to the elongated clusters and to the direction of shear. However, fluid percolation may still be possible in the perpendicular direction.

In the wider sense, complimentary results were achieved in the time-resolved characterization of pressure-solution processes (PSC). The adopted workflow provided new insights into the 3D evolution of pore space, and thereby transport properties, during ongoing pressure-solution processes. The strong reduction in bulk porosity and pore connectivity within the phyllosilicate layer indicates that phyllosilicates act as heterogeneities, which do not allow fluid percolation (cfr. chapter 4, section 4.6.3). However, fluids are still free to move and transport elements in the marginal pure NaCl layers. The increasingly flatter surface of the grains within the phyllosilicate layer induces an increase in grain contact areas and a reduction of the stress load, thereby lowering the chemical potential difference. Over time, this reflects a migration of the active dissolution front towards the marginal NaCl layers, where the chemical potential difference is higher. Here, the presence of pore space and pore connectivity allow fluid movement and transportation of ions in solution, thereby influencing transport distances (cfr. chapter 4, section 4.6.3). These results trigger important questions about the role of phyllosilicates in fault zones. The decrease in pore space and pore connectivity and the increased contact areas within this layer, which may act as barrier for fluid flow, may also drive fault healing (Hickman and Evans, 1995) (cfr. chapter 4, section 4.2.2).

The experiments further demonstrate that where incompressible structural heterogeneities are present (e.g. glass beads used as analogue material for quartz), the pore space retains its connectivity over time, and its reduction in volume is lower compared to that in the phyllosilicate layers. This means that fluid percolation is still possible, and that transport distances are limited to adjacent grains (Boer et al., 1977; Angevine and Turcotte, 1983) (cfr. chapter 4, section 4.6.4). However, transport distances progressively increase if the process is driven by enough chemical potential difference (cfr. chapter 4, section 4.6.4).

Furthermore, rock-salt is known to be characterised by very low permeability, which gives rock-salt its sealing capacity (Urai and Spiers, 2007; Ghanbarzadeh et al., 2014, 2015). The results herein reported confirmed that fluid percolation in rock-salt occurs even at conditions where the dihedral angles $\theta > 60^\circ$ and where fluid percolation is not allowed according to the static theory for texturally equilibrated porous media (Bargen and Waff, 1986; Lewis and Holness, 1996; Ghanbarzadeh et al.,
5.1 Final discussions

The percolation is due to a larger porosity content, and to deformation-assisted percolation mechanisms (in this case, PSC) at shallower depths and low T-P conditions. The presence of hydrocarbons within the rock-salt has already been recognized in the literature (Schoenherr et al., 2007; Ghanbarzadeh et al., 2015), opening new doubts on the properties determining the sealing capacity of rock-salt.

These key findings show the capability of µCT to capture changes to the dynamic evolution of porosity, reaction microfabric and transport properties during fluid-rock interaction. In the first case, the key findings showed that µCT can trace fossilised fluid pathways and determine the evolution of reaction microfabrics. The combination with EBSD analyses allowed determination of garnet deformation mechanism, opening new questions about its rheological behaviour in fluid-mediated systems. In the second case, bulk porosity, pore connectivity and pore microstructural changes (size and shape) were monitored over time during PSC. The combination with volumetric DIC provided information on the internal deformation and strain rates of the samples: the combination of these results with µCT quantitative and qualitative analyses offered new insights into the process, and enabled the inference of deformation mechanisms and dynamic transport properties.

These results also demonstrate that the 2D analyses are limiting, as these observations would not have been possible without the use of µCT. Despite this limitation, classical 2D analyses remain a powerful tool to determine microstructural and geochemical properties and in combination with µCT analyses can unravel the information hidden on the third dimension. Furthermore, the combination with 3D printing is offering the possibility to relate the microscale observation to the macroscale properties (Head and Vanorio, 2016).

5.1.1.1 NaCl as rock-analogue material

NaCl is commonly used to study PSC, together with other common soluble minerals such as KCl and K$_2$CO$_3$. The creep rates in these materials are much faster than in carbonates or silicates, for which PSC would be impossible to study within the time constraints of this project (Spiers et al., 1990; Gratier, 1993; Gratier et al., 2013). Natural rock-salt is composed by grains of halite (NaCl) and impurities. Fluids can be present as trapped in inclusions, grain boundaries or pores (Urai et al., 2008). The microstructural arrangement of NaCl grains and pores in rock-salt is naturally different from a sieved aggregate of NaCl grains, as the rock-salt has experienced diagenesis and has been deformed. In natural rock-salt the halite grains are not discrete, as in the case of sieved NaCl aggregates, which instead exhibit a higher
and more homogeneously arranged porosity. Moreover, in the experiments carried in this study, the grain size was uniform, while in natural rock-salt the grain size is variable (from micrometer to decimeter scale, cfr. Urai et al., 2008; Thiemeyer et al., 2015). However, the observed microstructures resemble the same characteristic features reported by previous studies in natural rock-salt (Urai et al., 1986), and it can be argued that sieved NaCl resembles an aggregate material, just with faster PSC kinetics: therefore NaCl can be used as rock-analogue material for rock-salt.

Ideal experiments to study PSC should be performed with carbonate rocks, as PSC is commonly observed in this type of rock. Carbonates rocks are characterised by the presence of a wide range of porosities, from micro- to macro- porosity. The presence or absence of these two types of porosity are very important when considering the Representative Elementary Volume (REV). The presence of macro- porosity would make small REV unrepresentative, introducing significant errors on the quantification of petrophysical properties (Hebert et al., 2015). More importantly, the segmentation algorithm may act differently depending on the size and the typology of the pore. Therefore, investigating the time-resolved evolution of transport properties during PSC in carbonates remains an open challenge. Studying PSC in a lab environment in carbonates is of course possible, if precautions are taken:

- an adequate REV needs to be chosen: this volume needs to be sufficiently small to allow high µCT resolution, and sufficiently large to include the range of porosity normally present in a carbonate rock (Regenauer-Lieb et al., 2013). There are different type of carbonate rocks, with different microstructures, therefore the choice of the carbonate rock is equally important. The type of REV varies accordingly to the type of carbonate rock. An oolitic limestone might be sufficiently permeable to allow PSC, and its microstructure offers many "point" contacts which can be easily monitored over time to study the evolution of the process.

- the sample needs to be heated to accelerate reaction kinetics and reduce the process time scale. In the case of calcite, solubility is recognized to be retrograde and to decrease with temperature (Ellis, 1959; Zhang et al., 2010). However, it is also shown that its solubility increases with salinity (Ellis, 1959; Zhang et al., 2010, 2011), accelerating PSC (Zhang et al., 2010, 2011).

- an increase in the load pressure to induce higher compaction rates.

In addition to these aspects, new segmentation/separation methods need to be considered which allow a precise quantitative analysis of the different ranges of porosity present in carbonates.
5.1 Final discussions

5.1.2 Evaluation of µCT techniques and advances

While X-ray microtomographic data allow for a complete visualisation of microfabrics and porosity in rocks in 3D (Denison and Carlson, 1997; Gualda and Rivers, 2006; Whitney et al., 2008; Wang et al., 2011; Goergen and Whitney, 2012; Sayab et al., 2014), the combination with established 2D microanalytical techniques critically provides new insights into tectono-metamorphic and fluid-rock interaction processes. In this way, internal characteristics of the samples (e.g. metamorphic microfabrics, porosity changes) can now be fully described in 3D. However, the extrapolation of information from 2D to 3D critically relies on:

1. a registration of the 2D data within the 3D dataset;

2. a correlation of real compositional data from the phases with intensities recorded in the 3D scalar fields that make a microtomographic data set (Gualda and Rivers, 2006);

3. an accurate segmentation of the relative phase volumes from the 3D datasets to allow for a further quantitative analysis.

Registration of the 2D data within the 3D dataset (1) is easily achievable thanks to the advance in image registration algorithms, which are now readily available. However, correlation of the real composition to the microtomographic intensities (2) and image segmentation (3) require more consideration. Instrument parameters and the reconstruction process also affect the intensity recorded for a particular location in the 3D data, as do partial volume effects and beam hardening artefacts (Ketcham and Carlson, 2001; Cnudde and Boone, 2013; Wildenschild and Sheppard, 2013; Leu et al., 2014; Maire and Withers, 2014). An internal study at APS-2BM-B showed that the imaging beamline apparatus used for the Kråkeneset gabbros investigation (chapter 3) reliably documents the interaction of samples with the incident X-ray beam with a minimum of variation in the instrument-sourced effects on the data (Dr. Xianghui Xiao, pers. comm.). The gridrec algorithm used to reconstruct 3D datasets from the radiographic projections is also robust and does not induce reconstruction-related artefacts in the data. However, the histograms of grey value distribution in the sµCT data (see chapter 2, section 2.4.1.2) point to the presence of a significant phase contrast signal (shoulder to the left of the atmospheric peak), which is persistent in all three datasets. Phase contrast produces strong bright and very dark anomalies around phase boundaries (Baker et al., 2012; Maire and Withers, 2014). These anomalies would affect any volumetric quantification. Volumetric quantifications can also be substantially affected by segmentation errors (Arns et al., 2002) (cfr. chapter 4, section...
4.6.7). The erosion/dilation procedure applied in both case studies to derive error bars covers these uncertainties (cfr. Liu and Regenauer-Lieb, 2011; Fusseis et al., 2012, chapter 2, section 2.4.3), allowing therefore an accurate 4D quantitative analysis.

However, in the case of carbonates or rocks with a more complex microstructure and heterogeneous porosity, erosion/dilation method may not be as conservative as expected. The erosion/dilation method does not recognize that segmented uncertainties are not evenly distributed across the image as they are affected by the 3D morphology of the segmented phase boundary. Therefore, methods that calculate probabilities on the uncertainties are more accurate where a heterogeneous microstructure is investigated. Thanks to the continuous development of image analysis, segmentation and separation algorithms are increasingly updated and improved, some of which include the calculation of probabilities as an estimation of these uncertainties. An example is the Trainable Weka Segmentation, available as segmentation plugin in ImageJ® (Schindelin et al., 2012). This plugin uses a machine-learning algorithm and segments materials based on features learned during a "training" process (Arganda-Carreras et al., 2014). Together to the final segmentation, the algorithm provides the user with a probability map, for each material segmented. In this way, the user can be confident on the choice made and can quantify uncertainties. Similarly, uncertainties have been recognized to play a major role also in modelling 3D geological structures by Wellmann and Regenauer-Lieb (2012). The authors proposed a theoretical solution to this problem through the concept of information entropy, which defines the sum of all probabilities for each outcome. The material to be investigated (regional model or microstructure) is divided into a regular grid, and for each grid cell the entropy is analysed. In this way, the uncertainties can be reduced by refining the judgements on them based on the information entropy. The same approach can be applied to the microscale investigation of tomographic images and subsequent upscaling (Regenauer-Lieb et al., 2013) (see section 5.2.3). These methods to map uncertainties are now available in open-source environments (ImageJ®, Python®, iPython® cfr. Pedregosa et al., 2012), and can be easily imported as script in image analysis software. This constitutes a new challenge for proprietary software like AvizoFire® (Avizo® in later editions), which lack of methods to calculate uncertainties in quantitative measurements as compared to open-source software.
5.2 Future challenges

5.2.1 Mapping chemical composition in 3D

The fluid-rock interaction puzzle still needs more investigations to better understand the geochemical and petrophysical processes operating on the microscale, and how these affect the dynamic transport properties within rocks. In this thesis, I have demonstrated the capability of µCT to map and quantify in 3D the evolution of porosity and reaction microfabrics, and determine how dynamic transport properties are affected. However, little can be said about element transport during fluid-rock interaction process. The exclusive use of µCT does not allow the quantification of element distribution in 3D, and compositional mapping is normally carried on 2D samples (EMPA, XRF, XRD). In recent years, however, with the advances of µCT and sµCT and improvement of experimental setup, there has been an increase demand for the investigation of element transport and distribution in 3D within rocks. There is a range of possibilities to determine chemical characterization in 3D using µCT. One way is using dual-energy CT (Tsuchiyama et al., 2013), in which the sample is scanned at two different energies, on either side of an element absorption edge. A similar approach was followed by Egan et al. (2015) using hyperspectral CT. In a laboratory CT scanner, the authors replaced the standard flat panel detector with a hyperspectral detector. These types of detectors are capable of recording or counting the number of X-ray photons of specific energies in each pixel during a particular exposure time (frame) and subsequently reconstruct the pixel photon energy spectrum for that particular frame (Egan et al., 2015). A different technique is combining µCT with analytical techniques that provide elemental characterization, such as XRF or XRD (De Samber et al., 2008; Bleuet et al., 2010; De Jonge and Vogt, 2010; Lombi et al., 2011; Uesugi et al., 2013; Wildenschild and Sheppard, 2013). At every rotational angle over a full 360° rotation, a full X-ray spectrum is recorded. The sinogram of each spectrum is then created, and reconstructed as 2D slice through filtered back-projection to obtain a 3D reconstructed dataset (Bleuet et al., 2010).

Another approach is directly obtaining the effective atomic number from the intensities of the grey values, which are related to the linear attenuation coefficient \( \mu \) (Spiers et al., 1990; Jussiani et al., 2016) (chapter 2, section 2.4.1.2). The advantage of this method is that it does not require to scan the sample at two different energy levels (dual-CT), or the use of synchroton-based µCT. With the fast improvement of machine-learning algorithms, it will be possible to integrate this theoretical solution with a segmentation algorithm that automatically maps the chemical composition in
the µCT images.

5.2.2 Future experiments

Previous studies have shown that pressure-solution creep rates are inversely proportional to the grain size (Paterson, 1995; Renard et al., 2001) (chapter 4, see section 4.2.1). Numerical modelling by Koehn et al. (2012) has shown that stylolites develop different morphologies depending on the grain size distribution present. In future experiments, it would be ideal to test these statements, to evaluate the effect of grain size and monitor the process over time. Particularly, I would like to test the effect of the presence of two different grain sizes in PSC and image the outcome in four dimensions.

Other interesting aspects of pressure-solution are represented by the re-precipitation sites and the nature of the fluid interface. The first aspect can be achieved by doping the fluid sequentially with elements that are readily incorporated in the precipitated minerals but modify the attenuation sufficiently to mark precipitation sites (e.g. REE). However, the doping technique would only work for phases into which the dopant is strongly partitioned (e.g. calcite) (Song et al., 2016), and not in NaCl, in which the fast dissolution-reprecipitation equilibrium would allow the dopant to be rapidly incorporated into all grains: any ion that could partition into the solid would rapidly coat all the mineral grains. Imaging in four dimensions the nature of the fluid interface is more challenging. The thickness of the fluid film along grain boundaries is on the scale of 10-100 nm (Dysthe et al., 2002; Gratier et al., 2013), therefore nanotomography instead of microtomography needs to be used. The nature of the fluid varies from a continuous fluid interface to an "island-channel" structure in which the fluid is in a dynamic state (see chapter 4, section 4.2.1.1) (Cox and Paterson, 1991; Gratier et al., 2013). At the very best, the reconstructed voxel size in nanotomography is 25 µm, which does not allow imaging the evolving morphology of the grain boundary, leaving the 3D characterization of the fluid interface an open challenge.

Further experiments with "dry" NaCl should be performed. Urai et al. (1986, 2008) reported that intracrystalline brine is present within "dry" halite. There are two types of "dry" NaCl: sieved NaCl grains from the chemical reagent container, and NaCl dried in a desiccated atmosphere. The new experiments should test if the presence of intracrystalline brine in both cases is sufficient to trigger pressure-solution processes.
5.2 Future challenges

5.2.3 Upscaling problem

Understanding the processes occurring at reservoir scale often requires numerical simulations that take into account the petrophysical properties of the rock at the microscale (Jackson and Blunt, 2000; Dvorkin et al., 2009; Varloteaux et al., 2013; Allan et al., 2015). Parameters like porosity and pore connectivity are very important to determine for this purpose, as well as their variability within the rock samples. The use of very small samples is often required in µCT to obtain a better and higher resolution. This is particularly relevant when the rock has a heterogeneous microstructure, in which micro- and macro-porosities are present, like in the case of carbonates, and for which small sizes of REV are unrepresentative (cfr. 5.1.1.1). Different methods should then be considered to also quantify micro- and macro-porosity changes in the rock.

Previous studies attempted to overcome this limitation by combining observations from multi-scale techniques and multi-resolution imaging (Bera et al., 2011; Dann et al., 2011; Peng et al., 2012, 2014; Prodanović et al., 2014; Hebert et al., 2015; Noiriel, 2015). A number of studies successfully related the microscale properties, imaged and quantified at the pore-scale through µCT, to the macroscale petrophysical characteristics measured in the lab (Lindquist et al., 2000; Arns et al., 2005; Knackstedt et al., 2008; Remeysen and Swennen, 2008; Blunt et al., 2013; Garing et al., 2014). Gouze and Luquot (2011) and Luquot et al. (2014) estimated porosity evolution in carbonates during dissolution using µCT and were able to derive permeability evolution as a function of porosity. Varloteaux et al. (2013) combined the results of µCT experiments with numerical modelling of reactive flow to better quantify dissolution regimes. Multi-scale approaches have also been adopted by Jackson and Blunt (2000), Dvorkin et al. (2009), and Allan et al. (2015), and reviews of upscaling may be found in Agar and Geiger (2014) and Hebert et al. (2015).

These approaches allow extrapolation and correlation of the observations made at nano- and micro-scale obtained with X-ray CT techniques to larger scales (e.g. thin section and hand specimen scale). However, the extrapolation of these observations to reservoir scale remains a challenging procedure. Numerical modelling of macroscale processes relies on a complete characterization of the physico-chemical properties of rocks at the microscale, as these constitute the input parameters for pore-scale modelling, which is needed to upscale the process (Agar and Geiger, 2014; Pak et al., 2016). Arns et al. (2001, 2004, 2005), Knackstedt et al. (2008), Dehghan Khalili et al. (2013a,b), and Hebert et al. (2015) obtained robust upscaling methods by directly computing petrophysical and transport properties from the µCT data.

Similarly, the methodologies adopted here aim to integrate the observations
obtained at different scales to fully characterize fluid-rock interaction. While microtomography data offered a 4D characterization of bulk porosity and pore connectivity, SEM and 3D-DIC provided microstructural investigation and strain rate measurements, respectively. The visual comparison between 3D-DIC outputs with the microtomographic data allowed identification of sites of strain localisation. Moreover, it enabled to discriminate what regulated the gradual slope evolution of the compaction curves. These informations, combined, represent the base for further modelling of the upscaling of fluid-rock interaction.
5.3 Concluding remarks

The use of rock-analogue material is limiting to some extent the investigation of geological processes. The very slow kinetics of deformation processes such as pressure-solution creep in carbonates rocks constitutes a problem to the investigation of these samples in a laboratory environment. Reaction kinetics can be speed up by an increase in temperature and load, however this increment may induce geochemical variations at the microscale, and running from room temperature to more elevated temperatures can also induce a change in reaction mechanism. While for the purpose of dynamic transport properties and fluid percolation this aspect may not constitute a problem, it is crucial for element transport and reaction front. Subsequently, investigating very slow kinetics in the lab and in short-term experiments remains an open challenge.

Despite this, the rapid advance in image data processing and experimental setup (see section 5.1.2) offers the possibility to expand the current knowledge of 4D studies of fluid-rock interaction from both the microstructural and geochemical point of view (see section 5.2.1). New experimental cells are continuously built to achieve conditions closer to reservoirs environments (Fusseis et al., 2014a; Renard et al., 2016). These experimental achievements provide the possibility to investigate geological processes in situ as close as possible to reality. The current field of image analysis is continuously expanding, so are the technologies, and the experimental investigations of geological processes. The combination of 2D and 3D data is easily available, so is the integration of analytical technique such as XRF and μCT to obtain simultaneously a range of information (microstructural and geochemical). Dynamic processes can be studied in situ, in real-time and with sub-micron resolution. In this sense, the 4D investigation of geological processes is a field which continues to improve and grow at a rapid pace.
References


171
References

Neuroscience 2014 Short Course 2 - Advances in Brain-scale, Automated Anatomical Techniques: Neuronal Reconstruction, Tract Tracing, and Atlasing, pp. 73–80.


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References


References


References


References

References


References


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References


References


Appendices
A. Supplementary material

A.1 Computing Resources

Different computing resources were used according to the type of analysis needed. Here a tabulation of the computing resources I used for each data, and the specific characteristics.
Appendix A. Supplementary material

<table>
<thead>
<tr>
<th>Computing Resources</th>
<th>Specifics</th>
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<tbody>
<tr>
<td>Scientific Linux Workstation</td>
<td>Intel Xeon 64-bit, 188.8 GB RAM, G. C. Gallium 0.4 on AMD PITCAIRN. Scientific Linux 7.2</td>
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<td>HP Reconstruction Workstation</td>
<td>CORE i7 Quad-core, 64-bit, 16 GB RAM, G. C. NVIDIA QUADRO K2000 2GB RAM</td>
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<td>Dell Workstation</td>
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<td>HP Workstation</td>
<td>Dual Xeon 16 cores, 64-bit, 256 GB RAM, G. C. NVIDIA QUADRO K5200 8GB RAM</td>
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**Servers**

<table>
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<tr>
<th>Terracorrelator</th>
<th>2 Large memory nodes (2TB), sharing 300 TB local storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eddie Cluster</td>
<td>4000 cores with up to 2 TB memory. Cluster uses Open Grid Scheduler batch system on Scientific Linux 7</td>
</tr>
</tbody>
</table>

**Datasets**

<table>
<thead>
<tr>
<th>Datasets</th>
<th>Computing Resource used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kråkeneset</td>
<td>Scientific Linux Workstation/Eddie Cluster Imagej on Scientific Linux Workstation</td>
</tr>
<tr>
<td>Pressure-solution data</td>
<td>Octopus Reconstruction on HP Reconstruction Workstation</td>
</tr>
<tr>
<td></td>
<td>Avizofire on DELL and HP workstation for image processing</td>
</tr>
<tr>
<td></td>
<td>TomoWarp on Terracorrelator</td>
</tr>
<tr>
<td></td>
<td>ID-Tracking performed by Edward Andó in Grenoble</td>
</tr>
</tbody>
</table>

**Table A.1:** The table lists the computing resources used for each data, and the specifics.
B. Supplementary material to Kråkeneset gabbros

B.1 Introduction

This appendix describes any additional material on the analysis of the Kråkeneset gabbros (chapter 3). Additional information includes complete EBSD results and a tabulation of the electron microprobe compositions. It also includes images on the 4-dimensional distribution of grain shapes (including Quant3D results and tables relative to the label analysis) and a small description of other segmentation methods that were not successful.
B.2 EBSD results

Figure B.1: EBSD results of low strain domain (sample 066B2). On EBSD-derived maps, high-angle boundaries (grain boundaries, misorientation > 10°) and low-angle boundaries (subgrain boundaries, misorientation > 3° and < 10°) were indicated with black and fuchsia lines, respectively. A) Phase map: Olivine (yellow), Plagioclase (white), Orthopyroxene (purple), Garnet (red), Hornblende (green). Red lines represent twinning boundaries in plagioclase. B) Inverse Pole Figure of Garnet in relation to the stretching lineation in the shear zone. Legend on bottom left corner. C) Local Misorientation Map, and legend, representing local misorientations from 0° (blue) to 9° misorientation (red). The arrow indicates the average local internal misorientation. D) Misorientation profile A-A’, location shown in figure C.
Appendix B. Supplementary material to Kråkeneset gabbros

Figure B.2: EBSD results of low strain domain (sample 066B2). E) Pole figures of Garnet. F) Pole Figure of Hornblende. G) Misorientation axis in crystal coordinates for low angle boundaries (3-10°).

Table B.1: Electron microprobe chemical compositions of oxides in garnets, used to calculate the x-ray absorption coefficients.
Appendix B. Supplementary material to Kråkeneset gabbros

Figure B.3: EBSD results of intermediate strain domain (sample 0617). A) Inverse Pole Figure of Garnet. Legend as in Figure B.1 B) Local Misorientation Map, and legend representing local misorientations from 0° (blue) to 9° misorientation (red). The arrow indicates the average local internal misorientation. C) Misorientation profile A-A’, location is shown in figure A. D) Misorientation profile B-B’, location shown in figure A. E) Pole figures of Garnet. The trace of the shear foliation is oriented NW-SE, pole figures are oriented with the trace of the mylonitic foliation parallel to the diameter (E-W). F) Misorientation axis of low angle boundaries (3-10°) in crystal coordinates.
Appendix B. Supplementary material to Kråkeneset gabbros

Figure B.4: EBSD results of high strain domain (sample 0618). A) Phase map: Grt (red), Am (green), Opx (blue), Bt (yellow). B) Local Misorientation Map, and legend representing local misorientations from 0° (blue) to 9° misorientation (red). The arrow indicates the average local internal misorientation. C) Inverse Pole Figure of Garnet. Legend as in Figure B.1 B. D) Misorientation profile A-A’, location is shown in figure C. E) Misorientation profile B-B’, location shown in figure C. F) Misorientation profile C-C’, location shown in figure C.
Figure B.5: EBSD results of high strain domain (sample 0618). A) Pole figures of Garnet. The trace of the shear foliation is oriented NNE-SSW, pole figures are oriented with the trace of the mylonitic foliation parallel to the diameter (E-W). B) Pole figures of Hornblende. C) Misorientation axis of low angle boundaries (3-10°) in crystal coordinates.
B.3 4D evolution of grain shapes

Figure B.6: Outputs of segmentation for olivine (green) and garnet (blue) grains, in the low strain domain (different viewing angles). The red arrows indicate olivine grains that are not completely enclosed by garnet coronas.

Figure B.7: Label analysis of intermediate strain domain after erosion. The large interconnected voxel cluster is now divided in disconnected subvoxel clusters. Long side 2630 µm.
Figure B.8: Results of Quant3D analysis on eroded data, from low strain (A) to high strain (C). With increasing deformation, garnet grains evolve from isodiametric shapes to more progressively discoid shapes as a result of the deformation.

Figure B.9: Tabulation of representative garnet structural formulae for the low (066B2) and high (0618) strain domain obtained from the microprobe analyses at the University of Münster.
### Table B.2: Frequency distribution data for non-eroded data.
The first column of each dataset refers to absolute frequency, the second one to the cumulative frequency relative to the total amount of garnet in each sample.
### Table B.3: Frequency distribution data for eroded data.

The first column of each dataset refers to absolute frequency, the second one to the cumulative frequency relative to the total amount of garnet in each sample.

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**Tot. Grt Vol.** 2.89E+08 5.83E+08 1.13E+09
B.4 Attempted segmentation methods

B.4.1 Indicator Kriging (IK)

A first attempt in segmenting garnet grains in the Kråkeneset gabbros was done using *Indicator Kriging* (IK) (Oh and Lindquist, 1999). This method is composed of two image processing steps, a thresholding step, in which threshold values are chosen to identify the populations of the image, and a kriging step, in which unclassified voxels are assigned to one of the phases through a probability function. It also includes two major filtering steps, one after the thresholding step, and one after the kriging step to guarantee smoothness in the resulting image. Despite garnet and olivine were clearly distinguishable in the original data, the outputs of IK included both phases, hence introducing substantial miscalculations in the garnet segmentation and quantification.

![Figure B.10: Results of indicator kriging for olivine, low strain domain of Kråkeneset gabbros.](image)

*a) Output of indicator kriging: IK is not able to discriminate between olivine and garnet. B) Segmented garnets after Statistical region Merging (SRM) and post-processing using the workflow outlined in chapter 2, section 2.4 (Figure 2.17). These results are neater and cleaner compared to IK results.*

B.4.2 Blob3D

*Blob3D* is a image analysis software, developed by Ketcham, 2005a,b. The software includes tools for image segmentation as well as tools for separation and characterization of segmented phases. The characterization of segmented grains in *Blob3D* is similar to what is implemented in many other software, such as in *AvizoFire*. I attempted to segment garnet grains in *Blob3D* by global thresholding, but as it turned out for the previous attempts also in *AvizoFire*, this algorithm is not powerful enough due to the strong overlapping of the mineral phases. Data were therefore segmented using the approach outlined in chapter 2, section 2.4 (Figure 2.17).
Characterization of garnet grains was also attempted in Blob3D®: however, due to the large size of the datasets, which require lot of computational time and memory, the characterization of garnet was conducted through AvizoFire® using Label Analysis operator.

**Figure B.11:** Outputs of blob3D segmentation. Left: Outputs of Statistical Region Merging technique. Right: Outputs of a cropped volume in Blob3D: garnet segmentation is unsatisfactory and inaccurate compared to the output of the adopted workflow.
Appendix C. Supplementary material to pressure-solution data

C. Supplementary material to pressure-solution data

C.1 Introduction

This appendix describes any additional material on the analysis of the pressure-solution data (chapter 4). The additional information includes the results of pore shape and pore orientation analyses for different sample compositions with increasing strain.
Appendix C. Supplementary material to pressure-solution data

C.2 Pore evolution during ongoing pressure-solution processes in NaCl
Appendix C. Supplementary material to pressure-solution data

Figure C.1: Flynn diagrams for increasingly shortened datasets: A) NaCl-biotite, first run; B) NaCl-glass beads first run; C) NaCl-biotite-glass beads. Vertical shortening in percentage.
Figure C.2: Flynn diagrams for pure NaCl and NaCl-biotite samples, compacted for 2465 hours, for increasing compaction: A) pure NaCl sample; B) NaCl-biotite sample; C) Flynn diagram for central biotite layer in NaCl-biotite sample; D) Flynn diagram for marginal NaCl layers in NaCl-biotite sample. Vertical shortening in percentage.
Appendix C. Supplementary material to pressure-solution data

Figure C.3: Flynn diagrams for pure NaCl and NaCl samples, compacted for 2465 hours, after Border Kill operator in Avizo. Vertical shortening in percentage.

Figure C.4: Pores orientations for increasingly shortened datasets: A) NaCl-biotite sample (compacted for 444 hours). B) NaCl-glass beads (compacted for 444 hours). Vertical shortening in percentage.
Figure C.5: Pores orientations for samples compacted for 2465 hours, for increasingly shortened datasets: A) Pure NaCl, B) NaCl-biotite, C) NaCl-glass beads-biotite. Vertical shortening in percentage.
Figure C.6: Pores orientations in central biotite (A) and pure NaCl marginal layers (B) for the NaCl-biotite samples, compacted for 2465 hours. Vertical shortening in percentages.