DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE **RAPPORT 2020/30**

Capture, Storage and Use of CO_2 (CCUS)

Seal capacity and geochemical modelling

Niels Springer, Knud Dideriksen, Hanne D. Holmslykke,
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Content

Dansk Sammendrag

Den nedre jurassiske Fjerritslev Formation er den primært forseglende bjergart for den underliggende Gassum Formation, hvori CO_2 tænkes lagret. Fjerritslev Formationen består af en sortgrå relativ ensartet lagpakke af marine skifre, der er svagt karbonatholdige. I lagpakken forekommer indslag af grovere lag såsom silt og sand. Formationen er til stede over det meste af den danske del af Det Norsk-Danske Bassin, begrænset mod nordøst af den Fennoskandiske Forkastnings Zone og mod syd af Ringkøbing-Fyn Højderyggen. Den maksimale tykkelse er mere end 1000 m i Fjerritslev Truget og formationen forventes at være ca. 500 m tyk over det meste af Sjælland. De forseglende egenskaber af Fjerritslev Formationen har mest være studeret i Stenlille området, hvor den er udviklet som en > 200 m tyk muddersten med indslag af porøse sandende og siltede lag, der deler den i en nedre or øvre forseglende enhed.

Ren og tør CO_2 anses normalt som værende ikke-reaktiv over for mineraler. Specielt for forseglende bjergarter gælder imidlertid, at tør super-kritisk CO_2 kan reagere med den forseglende bjergart og dermed ændre seglets egenskaber. Således kan tør super-kritisk CO_2 forårsage krympning af vandbærende lermineraler i seglet, såsom smektit, hvilket kan skabe nye eller udvide eksisterende sprækker i seglet og derved forøge den opadgående transport af CO_2. Derudover kan interaktionen mellem tør super-kritisk CO_2 og seglet føre til dannelse af karbonater og mobilisering af sporstoffer, omend i begrænset omfang sammenlignet med reaktioner forårsaget af CO_2 opløst i formationsvandet.

En del af det injicerede CO_2 opløses i formationsvandet, hvorved formationsvandets pH-værdi falder. Dette fald i formationsvandets pH kan øge opløsningen af den forseglende bjergart. For forseglende bjergarter er de mest relevante reaktioner opløsning af karbonater, let reaktive silikater såsom K-feldspat, og lermineraler. Opløsning af reaktive lermineraler og silikater, som eksempelvis K-feldspat og chlorit, er forbundet med sekundær udfældning af andre mineraler, f.eks. karbonater og kaolinit og forventes derfor kun at have mindre effekt på de forseglende egenskaberne. Opløsning af karbonater antages derimod ikke at være ledsaget af udfældning af sekundære mineraler, og derfor kan seglets porøsitet og permeabilitet øges, hvilket kan reducere de forseglende egenskaber. Da reaktionsfronten kun forventes at bevæge sig en brøkdel af seglets tykkelse ind i seglet, forventes opløsning af karbonater generelt ikke at kompromittere lagringsstedets sikkerhed. I forbindelse med denne rapport er der udført indledende modelberegninger til vurdering af Fjerritslev Formationens respons på indtrængning af super-kritisk CO_2 for at teste om forsegling eller udvidelse af tryk-relaterede sprækker kan opstå. Disse beregninger indikerer, at der kan forventes betydelige volumenændringer, hvis undermættet CO_2 fører til udtørring af seglet. Yderligere undersøgelser er dog nødvendige for at teste, om dette kan kompromittere lagringskompleksets sikkerhed.

Med hensyn til mulige kemiske reaktioner mellem danske forseglende bjergarter og CO_2 er der kun udført en eksperimentel undersøgelse (AQUA-DK projektet). I denne undersøgelse indeholdt prøven fra Fjerritslev Formationen kun små mængder kalcit, dolomit og siderit, som ikke viste klare tegn på opløsning under laboratorieforsøgene.

Anbefalinger til fremtidige undersøgelser

Den nuværende regionale viden om Fjerritslev Formation peger alle på dens gode stærke forseglende egenskaber, men fremtidige områdespecifikke data skal indsamles for at sikre og validere vurderingen.

Primære fokusområder børe være:

Studie fokuseret på variationer af bjergarstyper i Fjerritslev Formationen da den indeholder både forseglende og ikke-forseglende lag. Dette betyder både en geologisk model for disse forekomster der kan tilpasses bestemte områder og bestemmelse/modellering af de specifikke bjergarstypers egenskaber.

Permeabilitet af Fjerritslev Formationen er kendt fra få målinger som er lave til moderat høje, hvilket kan vise sig at udgøre en risiko for forseglingen. Yderligere studier og forbedrede modeller herfor skal foretages. Specifikke målinger af permeabiliteten overfor CO_2 samt evt. effekter af udtørring af skiferen af CO_2 bør også studeres.

De mekaniske egenskaber af Fjerritslev Formationen samt undergrundens stressfelt er dårligt kendt både regionalt og lokalt. Data fra udførte brøndtests af trykopbygningen samt studier af borehulsstabiliteten i eksisterende brønde indenfor det dansk område anbefales for at etablere en regional forståelse hvorfra lokale modeller kan etableres.

For at øge vores forståelse af de specifikke hydro-geokemiske reaktioner mellem CO_2 og den forseglende bjergart over Hanstholm- og Havnsø-strukturerne foreslås en tretrinsplan:

- Trin 1, der udføres indledende hydro-geokemisk modellering for at definere kritiske ubekendte, der skal kvantificeres eksperimentelt og danne grundlag for optimal design af laboratorieforsøgene.
- Trin 2, yderligere avancerede laboratorieundersøgelser af den forseglende bjergart udføres, samt stedspecifikke geokemiske laboratorieforsøg rettet mod besvarelse af de specifikke videnskabelige spørgsmål, der er rejst i trin 1.
- Trin 3, den endelige geokemiske modellering til at kvantificere forseglingens ydeevne ved lagring af CO_2.

Summary

The Lower Jurassic Fjerritslev Formation is the primary seal to the underlying sandy Gassum Formation reservoir. The Fjerritslev Formation consists of a dark grey, relatively uniform succession of marine, slightly calcareous mudstones, with varying content of silt and sandstone laminae. The formation is present over most of the Danish part of the Norwegian-Danish Basin, bounded to the northeast by the Fennoscandian Border Zone and south by the Ringkøbing Fyn High. The maximum thickness of more than 1000 m is reached in the Fjerritslev Trough and is expected to be c. 500 m thick across Sjælland. The sealing capacity of the Fjerritslev Formation has mostly been studied in the Stenlille area. Here, the seal is a > 200 m thick mudstone with interbedded porous sandy-silty layers that divides the seal into a lower and upper seal unit.

This report presents the main seal rock properties of the Fjerritslev Formation, including a specific geochemical analysis assessing the reactivity of the Fjerritslev Formation towards CO_2 when sealing a CO_2 storage site over geological time.

The mineralogy of the Fjerritslev Formation has been treated in several publications. The non-clay sized part of the rock is quartz dominated with kaolinite and in some intervals illite and smectite as the dominant clay-size mineral. Authigenic/diagenetic minerals include pyrite, calcite and siderite. Petrophysical data including porosity, permeability and mercury injection data are available from a few samples of the Fjerritslev Formation. The sample analyses are sparse mostly due to lack of good quality cores and of previous erroneous analyses. Average porosity is 11%; air-permeability is 160 µD and mercury injection entry pressure ranges from 60 to 110 bar (air-brine system). Air permeability and mercury injection data are less reliable due to the dry condition of the samples during measurement. Very few liquid permeability data are available; one liquid (brine) permeability measured at *in situ* conditions in a massive mudstone layer from Stenlille reached a value of 3 nD which is similar to the best petroleum caprocks known, a few other overburden measurements gave liquid permeabilities around 200 nD.

A specific CO_2 seal capacity test from Stenlille relative to gas and supercritical (dense) CO_2 ($scCO_2$) provided entry pressures of 50 and 70 bar respectively for a massive mudstone layer in the Fjerritslev Formation. This shows that the seal will hold a vertical column of supercritical CO_2 of at least 1000 m, i.e. much more than the thickness of the underlying Gassum Formation reservoir anywhere in the Danish Basin. However, the assumption is that the result for the Stenlille area can be generalised for the entire Fjerritslev Formation. It is well known, that the Fjerritslev caprock is heterogeneous in places, and therefore this subject needs more attention, and for each CO_2 storage complex a careful and through study of the caprock is essential to demonstrate the seal capacity and integrity.

Traditionally, pure and dry CO_2 is considered unreactive in the subsurface. However, for caprocks, dry $scCO_2$ may interact with the caprock and possibly change the properties by causing shrinkage of water-bearing clays such as smectite in the caprock, which may create new or enhance existing fractures in the caprock thereby facilitating upward migration of CO_2. Furthermore, dry $scCO_2$ interaction with caprock may lead to carbonation and mobilization of trace elements, although to a limited extent compared to the reactions caused by CO_2 dissolved in the formation water.

Part of the injected CO_2 will dissolve in the formation water, thereby lowering the pH of the water. This decrease in pH may facilitate dissolution of the caprock itself. Most relevant for caprocks are dissolution of carbonates, readily reactive silicates such as K-feldspars and clay minerals. Dissolution of reactive clay minerals and silicates such as K-feldspar and chlorite is associated with secondary

precipitation of other minerals e.g. carbonates and kaolinite and therefore is expected to have only minor effect on the caprock properties. Dissolution of carbonates on the other hand is not assumed to be followed by precipitation of secondary minerals and therefore the porosity and permeability of the cap rock may increase, which may reduce the cap rock properties. Since the reaction front is expected only to migrate a limited distance into the caprock, then dissolution of carbonates is generally not expected to compromise the storage site security. In this study, preliminary modelling to assess the response of the Fjerritslev Formation to invasion of $scCO_2$ has been performed to test if sealing or expansion of pressure induced fractures occur. These calculations indicate that substantial volume changes can be expected if sub-hydrated CO_2 leads to drying of the caprock. Further studies are, however, needed to test if this may compromise the security of the storage complex.

Only one experimental study has been carried out (the AQUA-DK project) to investigate possible chemical reactions of Danish cap rocks with CO_2. In this study the Fjerritslev Formation sample contained only small amounts of calcite, dolomite and siderite which did not show clear signs of dissolution during the laboratory experiments.

Recommendation for future work

The current regional knowledge of the Fjerritslev Formation shows all positive indications of its strong seal capabilities, but future site-specific data needs to be collected to ensure and validate the regional character and properties. This is relevant both for petrophysical and hydrogeochemical data.

To increase our understanding of the specific hydrogeochemical reactions between CO_2 and caprock above the Hanstholm and Havnsø structures, a three-stage plan is proposed:

- Stage 1 preliminary modelling is performed to define critical unknowns that should be quantified experimentally and provide the basis for design of the laboratory experiments. As part of this first stage, experimental work on existing core material will also be performed.
- Stage 2, additional advanced laboratory caprock studies will be performed as well as geo-chemical laboratory experiments directed at answering the specific scientific questions raised in stage 1.
- Stage 3, the final geochemical modelling to quantifying the performance of the seal during storage.

To focus our recommendations for future work on petrophysical knowledge, we have followed the caprock integrity analysis and risk assessment techniques developed by Bruno et al. (2014) and evaluated the Fjerritslev Formation accordingly (Table 0.1). The risk factors include 18 different parameters of which five have been discussed here and evaluated either with a reasonable certainty or provisionally pending on more data and analyses. The evaluation show that none of the evaluated parameters fall within the high-risk category of Bruno et al. (2014) and that most of the evaluated risk factors fall within the low to medium risk group. Most of the risk parameters that have been assigned a medium risk need, however, additional analysis and characterisation before final evaluation can be made.

Rock type variation in the seal

The Fjerritslev Formation for most of the Danish subsurface has been evaluated based on data from Stenlille for now (Table 0.1). The Fjerritslev Formation here scores with low to medium risks for its geological data such as thickness and complexity, However, the abundance of silty beds may pose a risk to seal capacity. These aspects should still be evaluated in future project especially as these a known to vary with geographical position.

Permeability

For data that we currently have obtained then permeability appears to pose a moderate risk and future studies should be directed towards this aspect since it may pose a threat to the site. More specific CO_2 injection studies is also recommended to be made, preferably from new site-specific wells.

Mechanical strength and aspects related to the subsurface stress field

The mechanical strength and subsurface stress field are currently unknown aspects of the seal capacity analysis treated here and are thus marked with blue in Table 0.1. We have an indication of the dynamic properties calculated from the sonic velocities, that the Fjerritslev Formation is a medium stiff shale, but this needs further analysis from wire-line logs supplemented by core analysis – both site-specific as these properties may vary. Also, site-specific stress-strain relationships should be worked out. Presently, we only have data from leak off tests from Stenlille but none on a regional scale.

Site-specific research and pressure testing in wells

Future site-specific research on the Fjerritslev Formation should focus on new core material of the caprock. Advanced laboratory caprock studies should be executed as soon as possible after the core has been cut to avoid damages to the samples. Likewise, advanced rock mechanics studies on fresh samples should be carried out immediately after the core has been cut. We also recommend advance pressure testing in the well to establish the rock strength and features such as the fracture propagation pressure.

Table 0.1. *Risk matrix for the cap rock of the Fjerritslev Formation in Denmark. Risk factors according to Bruno et al. (2014). Green colour indicate that the risk factor has been evaluated with a reasonable confidence. Note that not all risk factors have currently been evaluated or are too site specific to allow for a general evaluation.*

Risk factor	**Risk factor value ranges**		
	High risk	**Moderate risk**	**Low risk**
Lateral extension of the storage zone/formation depth	< 25	25–100	> 100
Storage zone thickness/storage zone depth	> 0.5	0.1–0.5	< 0.1
Stress regime	Compressional	Transform	Extensional
Caprock strength	Weak	🟩 Moderate	🟩 Strong
Caprock thickness	≤ 3 m	3–30 m	🟩 ≥ 30 m
Fault boundaries	Multiple	One	≥ 30 m
Natural seismicity	High	Moderate	Low
Number of caprocks	No	One	🟩 Multiple
Maximum formation pressure/formation depth	≥ 0.75	0.625–0.75	≤ 0.625
Desired maximum formation pressure/discovery pressure	≥ 1.5	1.25–1.5	≤ 1.25
Well density	> 15 km^2	5–15 km^2	< 5 km^2
Number of uncased wells/total number of wells	> 0.6	0.2–0.6	< 0.2
Temperature difference between the injected CO_2 and the ambient storage zone temperature	≥ 60°C	30–60 °C	≤ 30 °C
Caprock heterogeneity	Significant	🟩 Moderate	Strong
Caprock permeability	> 10^{-15}m^2	🟩 10^{-18} – 10^{-15} m^2	< 10^{-18} m^2
Caprock lateral extend/storage zone thickness	< 25	25–100	> 100
Caprock dip	≥ 8°	2°–8°	≤ 2°
Minimum horizontal stress/vertical stress (stress ratio)	< 0.55	0.55–0.65	> 0.65

1. Introduction

The growing concern of global warming caused by large CO_2 emissions to the atmosphere has increased the focus on geological storage and utilization of CO_2 as possible mitigation measures for reducing the emission to the atmosphere. Several potential CO_2 storage sites have been identified in the saline sandstone aquifers in the deep subsurface of Denmark. Two of these are the Hanstholm and Havnsø structures, where the primary storage formation is the Gassum Formation sandstones, sealed by the Fjerritslev Formation mudstones. This report focuses on a description of the Fjerritslev Formation seal properties, and further describes potential geochemical reactions between CO_2 and caprock minerals. Recommendation for future site-specific studies is presented to ensure and validate the regional character and properties.

2. Seal description

A seal (or caprock) is an underground tight rock formation or layer that prevents fluid flow (salty pore water, gas or hydrocarbons) from a deeper level reaching the groundwater zone or the Earth surface. Seals are primarily mudrocks or evaporites and they form the main regional caprocks to natural oil and gas reservoirs as well as commercial aquifer gas storage sites (Aplin et al., 1999, Corcoran and Doré, 2002). The terms “shale” and “mudstone” are used in this task as synonyms for mudrock – a fine-grained sedimentary rock with a high content of silt and clay size particles (Lundegard and Samuels, 1980). Evaporites can be halite (rock salt), anhydrite or fine grained lithologies cemented with chlorides, sulfates or carbonates (calcite, dolomite). The texture, grain size distribution and packing of grains and the mineralogy determine the quality of the caprock with respect to entry pressure, flow and potential chemical reactions in the system composed of CO_2 – pore water – rock minerals.

2.1. High quality caprocks

The properties of very high-quality seals are known mainly from oil and gas reservoirs where caprocks remain tight for more than 10^7 years except for accidental open fractures that may heal again after a shorter period. However, the caprock matrix remains tight. Good petroleum caprocks are known to have permeabilities in the nano Darcy (nD) range (<10 nD) and high gas threshold pressures (> 7 MPa) (Keelan, 1982), but caprocks of lower quality may potentially be suitable for CO_2 sequestration, cf. below.

The most important control on the seal efficiency of a mudrock is the pore throat size because it controls permeability and capillary entry pressure (Katsube and Williamson, 1994). The pore throat size is controlled mainly by the grain size distribution and compaction (Heling, 1970; Katsube and Williamson, 1994). Thus, the presence and amount of clay size particles can reduce permeability very significantly as shown by Yang and Aplin (1998) and Dewhurst et al. (1999). In these studies, it was concluded that clay rich and calcareous shales were excellent seals due to their small pore throats (< 15 nm) and it is therefore an important parameter in evaluating the sealing capacity of a caprock.

In a CO_2 sequestration context, calcareous shales may not unconditionally be an ideal seal due to mineral reactions taking place between CO_2 dissolved in the pore fluid and reactive minerals like carbonates as the work on the EU Weyburn Monitoring Project (Riding and Rochelle, 2005) has shown. Furthermore, Krushin (1997) observed that organic shales offered a lower seal quality due to matrix shrinking during subsidence and hydrocarbon generation that created enlarged entry pressure pore throats in the organic rich shales.

2.2.1. Seal ample for CO_2 sequestration

While petroleum caprocks may effectively have been tight over geological time scales, this may not necessarily be a condition for a CO_2 storage site. Thus, a case for a sufficiently tight CO_2 repository must consider a realistic residence time scenario for the stored CO_2.

Dissolution in the pore fluid and trapping of CO_2 in newly formed minerals may take place in an aquifer storage in less than 5 000 years (Lindeberg and Bergmo, 2002; Riding and Rochelle, 2005; Holloway *et al.*, 2006). Based on a general climate model, Lindeberg (2002) concluded that a residence time of at least 10 000 years is needed to prevent injected CO_2 from re-entering the atmosphere-ocean system. This implies that the quality of a caprock above a CO_2 repository may not be of the same high standard as for a petroleum reservoir.

Lindeberg and Bergmo (2002) also studied volume diffusion in porous rocks. With a bulk diffusion coefficient of 2×10^{-9} m^2/s CO_2 diffusion in the aqueous phase (because CO_2 is slightly soluble in brine) to bypass a reasonably thick caprock unit is a slow process taking 10^5-10^6 years or even longer. With a time scenario of 10 000 years diffusion within and through the caprock is therefore not important in CO_2 sequestration.

2.2.2. Risk notes

To reduce the risk of seal failure it is generally assumed that CO_2 should be stored in a super critical (dense) condition ($T > 31$ °C and $P > 7.4$ MPa). This is assumed to correspond to at least 800 m below ground level. Likewise, it is preferable that the thickness of the seal is ≥ 30 m to reduce the risk of small scale fractures compromising the caprock (Bruno et al. 2014).

Some operations may cause failure of the caprock seal, e.g. fracturing generated during an overpressure injection of fluids into the reservoir (Bruno et al. 2014). Fracturing and the effect on permeability, healing of fractures and numerical models including fracture flow have been treated in Wangen (2002), L'Heureux and Fowler (2002) and Gentier *et al.* (2000)**.** In tectonic active regions, faulting and reactivation of old faults and fractures may be another risk issue (Hollund *et al.*, 2002). Finally, leaking wells due to casing collapse or degraded casing cement due to aggressive CO_2 dissolved in the formation water may be other risk factors (Wilson *et al.*, 2011). A review of historical risk events related to storage of CO_2 and natural gas in abandoned oil and gas fields, aquifers and salt caverns can be found in Bruno et al. (2014).

2.3. Fjerritslev Formation

The Lower Jurassic Fjerritslev Formation forms the primary seal to the underlying sandy Gassum Formation reservoir. The Fjerritslev Formation is present over most of the Danish part of the Norwegian-Danish Basin, bounded to the northeast by the Fennoscandian Border Zone and to the south by the Ringkøbing-Fyn High (Figure 2.1 and 2.2). The formation is also present south of the Ringkøbing–Fyn High. The formation has a variable thickness due to Mid Jurassic uplift and erosion in the south-western and central parts of the Danish Basin and above salt structures (Fig. 2.2.). The maximum thickness of more than 1000 m is reached in the Fjerritslev Trough (Michelsen 1975, 1978, Michelsen et al. 2003, Nielsen 2003).

The formation consists of a dark grey, relatively uniform succession of marine, slightly calcareous mudstones, with varying content of silt and sand beds and laminae. Siltstones and fine-grained sandstones are locally present being most common in the north-eastern, marginal parts of the Danish Basin (Michelsen 1975). The mudstones have a variable content of pyrite and organic matter; in the upper part of the formation (F-III and F-IV members) contents around and even exceeding 3 wt.% TOC have been measured (Petersen et al., 2008). The formation is characterised as an organic-rich shale with a poor to excellent oil source rock potential. However, the wells studied from the Danish Basin have shown the mudstones of the Fjerritslev Formation to be thermally immature with no petroleum generation expected to have occurred (Petersen et al., 2008), which is an advantage from a caprock perspective (c.f. Krushin, 1997).

The Fjerritslev Formation is formally divided into four members F-I to F-IV by Michelsen (1978). The lower F-I member, directly overlying the Gassum Formation, consist of marine mudstones with an average thickness of 150 m. In the above lying F-II member, the sedimentation changes to more silty-sandy heteroliths, later followed by a fine-grained mudstone making up more than 100 m in the central part of the Danish Basin. The uppermost F-III and F-IV members are organic-rich marine mudstones with a few interbedded thin sandstones. The succession has a thickness of 100-400 m with thinning towards basin margins and above salt structures due to later uplift and erosion (Figure 2.2.).

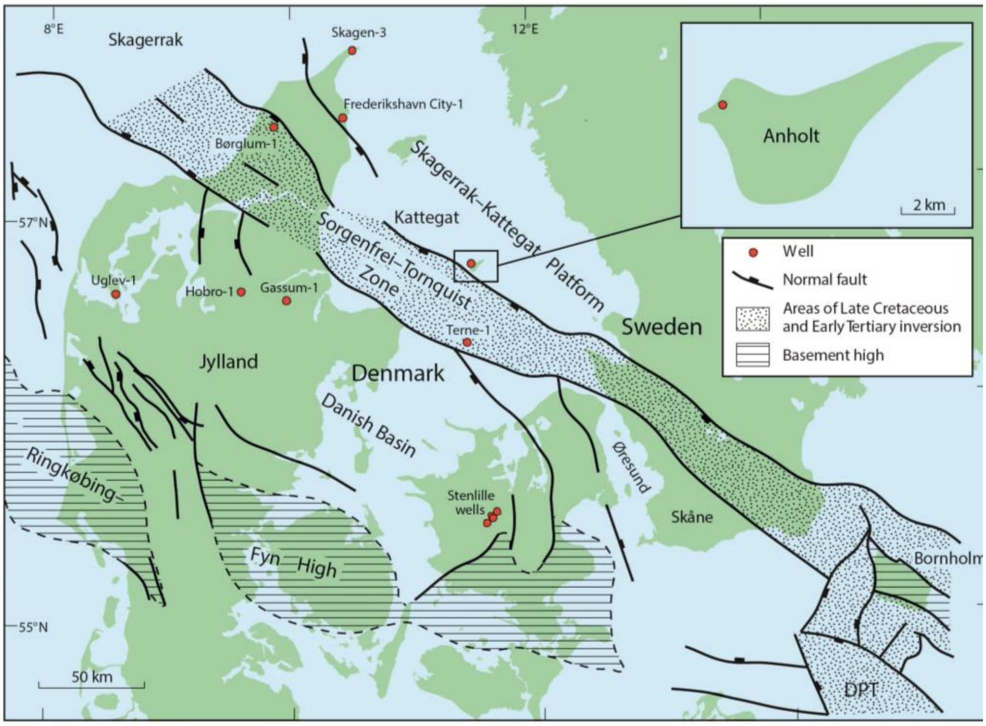


Figure 2.1. Outline of the Danish Basin with main structural elements and wells mentioned in text. From Nielsen et al.(2003).

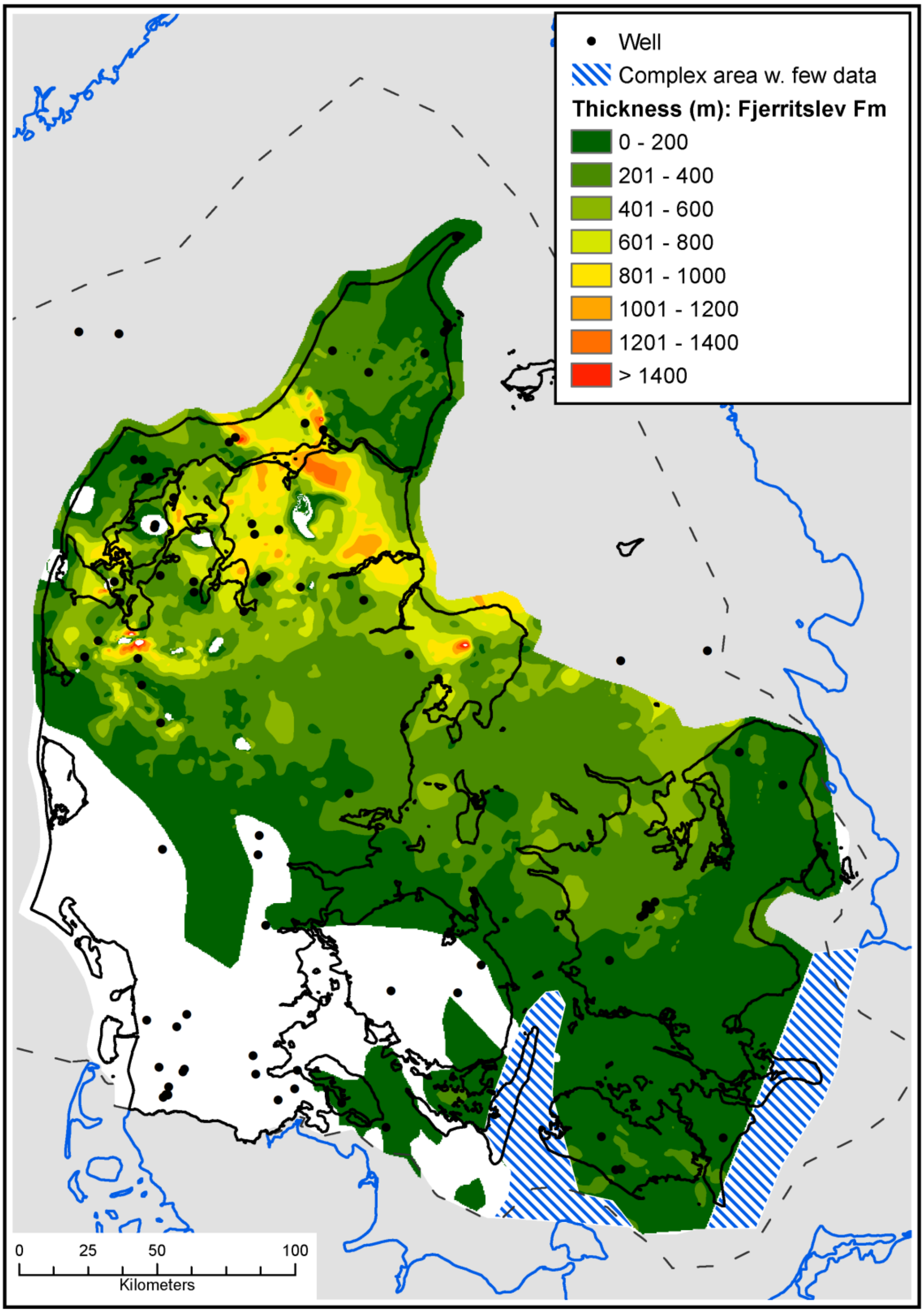


Figure 2.2. Thickness map of the Fjerritslev Formation in Denmark.

2.4. Mineralogy of the Fjerritslev Formation

The mineralogy of the Fjerritslev Formation has been treated in several publications. Schmidt (1985) investigated the Børglum-1 well situated just south of the Skagerrak-Kattegat Platform and found that quartz dominated the bulk rock composition and that kaolinite dominated the clay size fraction. In the overlying formation, smectite dominated the clay mineral assemblage. Semi-quantitative analysis of the bulk and clay fraction were also provided by Schmidt (1985). A commissioned semi-quantitative mineralogical study was carried out by Sedico (1989) on samples from the Stenlille area (Stenlille-4, -5 and -6). The study found that quartz dominated the bulk mineralogy of the Fjerritslev Formation with kaolinite and illite being the most frequent clay minerals; a compilation is given in Table 2.1 and 2.2. Nielsen et al. (2003) investigated the shallow boreholes on the island of Anholt, marginally placed between the Skagerrak-Kattegat Platform and the Sorgenfrei-Tornquist Zone (Figure 2.1.). The F-III and F-IV members of the Fjerritslev Formation where here cored and details of the mineralogy and geochemistry were presented. The mineralogy of the bulk samples comprised quartz and clay minerals. Authigenic/diagenetic minerals included pyrite, calcite and siderite. The clay size fraction was dominated by quartz, illite/muscovite and kaolinite; smectite increases downwards in the more fine-grained parts of the F-III member. Nielsen et al. (2003) noticed that the percentage of smectite normally increases with decreasing particle size and towards the basin centre. Japsen et al. (2002) claimed that a smectite-illite assemblage dominated the distal parts of the Fjerritslev Formation and that the high content of quartz is found in the vicinity of the Scandinavian basement. Springer et al. (2010) reported grain size, specific surface area and clay mineralogy for two samples from the Vedsted-1 and Stenlille-2 wells. The clay fraction in the Vedsted-1 is dominated by kaolinite, whereas illite, vermiculite, chlorite, and mixed-layer illite-smectite are present in small amounts. In the Stenlille-2 the clay fraction consists mainly of smectite, medium amounts of kaolinite, and small amounts of illite and chlorite.

Mbia et al. (2014) carried out a petrophysical and rock mechanical study mainly on cleaned and dried cuttings from two onshore localities in the Danish Basin (Stenlille and Vedsted). In total 22 samples representing the Fjerritslev Formation were taken from the Vedsted-1, Stenlille-2 and -5 wells and characterised for semi-quantitative mineralogy by XRD analysis. Although the results of the cuttings samples should be used with caution due to the possible contamination by drilling mud and by cavings from shallower intervals in the wells, the bulk rock composition in Table 2.3 is comparable to the findings by Sedico (1989) shown in Table 2.1 and 2.2 below. Semi-quantitative clay fraction XRD analysis of 20 cuttings samples from Fjerritslev Formation in the Margretheholm-1, Karlebo-1, Kvols-1 and -2 and Stenlille-2 wells were made by Vosgerau et al. (2016), where the clay mineral fraction is dominated by kaolinite and mixed-layer clays, whereas vermiculite, illite/mica and quartz are present in smaller amounts, and the bulk fraction furthermore includes feldspars, pyrite, calcite, siderite and ankerite. Only small variations occur in the clay mineralogy, and these variations may be related to placement in the basin in accordance with the different particle sizes of the clay mineral types. The analyses of bulk cuttings samples were compared to analyses of hand-picked mudstone cuttings fragments, showing that hand-picking gave better results since the most sandy/silty fragments and the identifiable cavings were discarded.

Table 2.1. Stenlille XRD bulk mineral composition for Fjerritslev Formation (Sedico, 1989). Composition is in % of total rock.

St. well	Core/Plug	Depth	Qtz	K-fsp	Plag	Cc	Dol	Sid	Py	Clay
no.	no.	[m]								min
4	C/2-113	1493.50	84	6	1	1	0	4	0	4
4	C/2-125	1497.50	74	3	6	0	0	3	0	14
4	C/3-404	1507.10	56	3	2	5	1	3	0	30
5	C/3-4	1532.30	81	12	2	tr	0	1	0	4
5	C/3-7	1533.30	66	3	3	0	0	6	0	23
5	C/4-509	1542.72	38	2	1	8	7	5	0	39
5	C/4-511	1549.04	33	2	2	2	2	4	0	55
6	C/1-6	1541.40	53	1	2	0	0	7	0	37
6	C/1-15	1544.40	65	9	1	0	0	4	0	21
6	C/1-620	1545.76	29	1	1	0	0	16	0	53
6	C/2-621	1556.94	40	3	2	2	2	3	0	48
6	C/2-622	1561.41	53	3	3	0	0	3	3	35

Abbreviations: Qtz – quartz, K-fsp – potassium feldspar, Plag – plagioclase, Cc – calcite, Dol – dolomite, Sid – siderite, Py – pyrite, Clay min – total clay fraction.

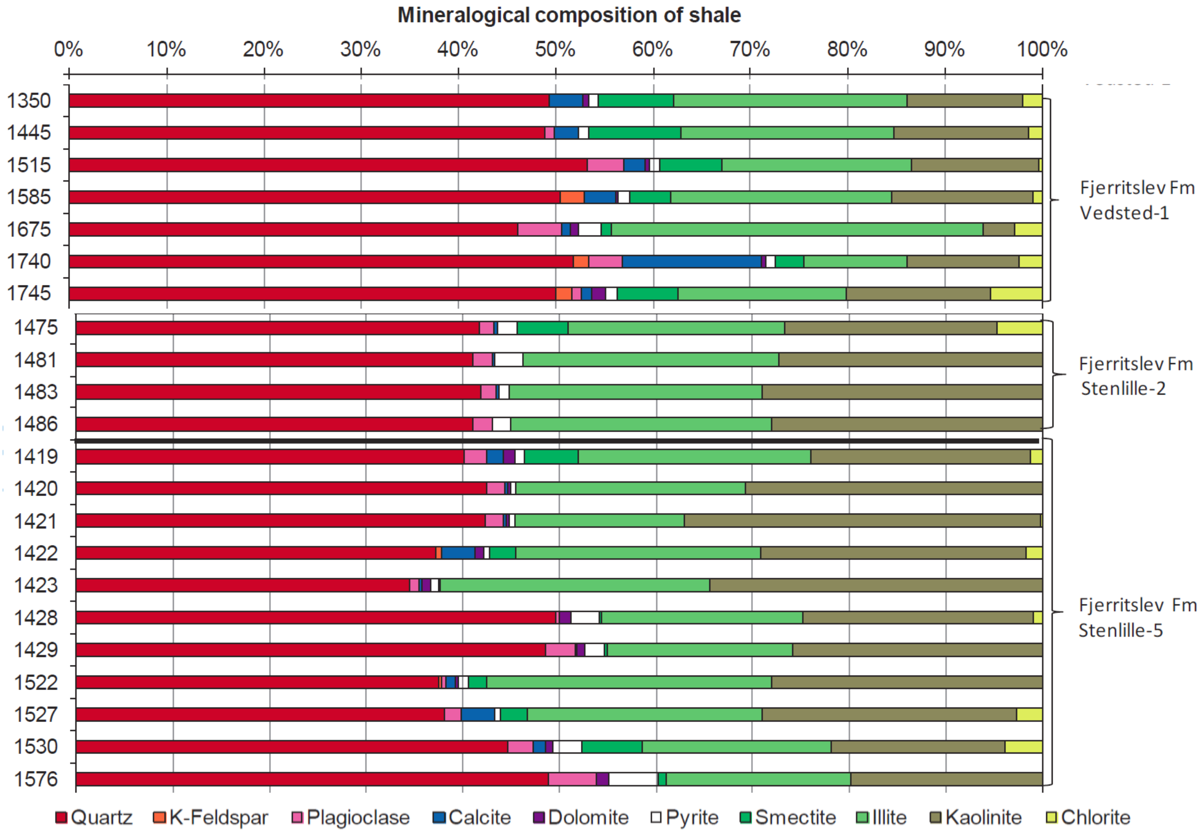
Table 2.2. Stenlille XRD clay mineral composition for Fjerritslev Formation (Sedico, 1989). Composition is in % of total clay fraction <2um.

St. well	Core/Plug	Depth	Chl	Kao	Ill	Mix/Smc	Qtz	K-fsp	Plag	Carb	Py
no.	no.	[m]	Clay minerals				Non-clay minerals				
6	C/1-6	1541.40	4	42	40	15	+	-	-	-	-
6	C/1-15	1544.40	2	53	32	13	+	-	-	-	-
6	C/1-620	1545.76	6	32	41	21	+	-	-	-	-
6	C/2-621	1556.94	4	49	41	6	+	-	-	-	-
6	C/2-622	1561.41	7	38	47	8	+	-	-	-	-

Abbreviations: Chl – chlorite, Kao – kaolinite, Ill – Illite, Mix/Smc – Mixed layers and smectite, + detected, - not detected.

In summary, the clay mineral assemblages encountered in the Fjerritslev Formation in the different studies are rather comparable, but variation occurs of which some may be related to different XRD interpretation procedures and the remaining variation must be related to source area, depositional environment and diagenesis. The clay mineral analyses are mostly carried out on samples from comparable depths, so the effect of diagenesis is not easily visible, although clay minerals are strongly dependent on temperature (e.g. Weibel, 1999), so additional analyses could focus on covering a larger depth span and geographical span. This should be possible since core material of the Fjerritslev Formation exists from several Danish onshore wells including Børglum-1, Farsø-1, Fjerritslev-1 and -2, Flyvbjerg-1, Frederikshavn-1 and -2, Gassum-1, Haldager-1, Horsens-1, Lavø-1, Rødby-1, Skagen-2, Stenlille, Sæby-1, Vedsted-1, Vemb-1, Vinding-1 and Aars-1. The effect of the maximum burial depth prior to Neogene uplift of the basin (Japsen et al., 2007) must also be considered since the maximum burial temperature determines the amount of diagenesis affecting the sediments.

Table 2.3. Bulk rock composition from XRD analysis of 22 cuttings samples representing the Fjerritslev Formation in the Stenlille and Vedsted locations (Mbia et al., 2014, their table 8). The silt fraction, mainly composed of quartz and feldspar, make up approx. 50% of the bulk rock. Vertical axis denotes sample depth (MD) in m.



2.5. Petrophysical data

Although the Fjerritslev Formation is present in almost all onshore deep Danish wells (Nielsen and Japsen, 1991), very few cores have been cut in the formation. A search in the GEUS archive and core analysis database have returned the Routine Core Analysis (RCA) porosity-permeability data presented in Table 2.4. Additional relevant seal capacity data from mercury injection tests on cleaned and dried samples have been included from the AQUA-DK Project (Springer et al., 2010). RCA porosity and gas permeability is carried out to the guidelines in API RP40 (1998), i.e. on small cylindrical plugs of 25 or 38 mm diameter drilled in horizontal or vertical direction relative to the bedding in the core, cleaned for formation water (brine) if possible, dried at a specified temperature and then analysed at room conditions for effective porosity by the He-injection method and permeability to N_2 gas at a confining stress of ≈2.8 MPa (400 psi). A few liquid permeability measurements to formation water (brine) are also included in Table 2.4. The Stenlille-2 data outlined in blue in Table 2.4 represent data measured at reservoir condition on preserved (fresh) core material, i.e. measured at the original temperature and pressure in the listed depth above the Stenlille gas storage (Springer et al., 2010). In a caprock context, the vertical permeability is most important, but some horizontal data are provided also as they are relevant in numerical simulation studies on the flow in the caprock. However, observe the evaluation of data quality in the section below.

A commissioned caprock study carried out by Redwood Corex Services (1989) measured liquid permeability and N_2 gas break-through pressure on mudstone samples from Stenlille-4, -5 and -6. However, the analytical procedures applied suggest that the samples were damaged during measurement, and the results are thus not reliable.

The study by Mbia et al. (2014) referenced in the mineralogy section measured porosity, permeability and compressibility of the Fjerritslev Formation in the Vedsted and Stenlille areas. Sampling was based on uncleaned cuttings from 3 wells that, in a comprehensive study, were analysed for porosity by different techniques including the conventional He-porosity (API RP40, 1998), mercury injection (MICP) porosity and nuclear magnetic resonance (NMR) porosity; a summary is listed in Table 2.5. Estimates of the permeability were indirectly derived from elastic moduli (velocity of sound data), combined MICP + NMR data, and specific surface area (BET) measurements + Kozeny's equation for shales. NMR data was obtained on a few natural state plugs drilled from preserved core sections in Stenlille wells. These plugs were further used in a direct measurement of liquid permeability from constant rate of strain (CRS) tests at overburden conditions. Results are listed in Table 2.5. Uniaxial static and dynamic compressibility was also measured on the natural state mudstone plugs from the Stenlille wells by Mbia et al. (2014b).

2.6. Evaluation of data quality

The data presented in Table 2.4 are of varying quality due to the history and inevitable core handling. The Børglum, Farsø and Vedsted wells were drilled many years ago and core material was left to dry in the GEUS core store. Due to salt precipitation from the drying core and the effect of humid conditions in the store, delicate clay minerals like mixed-layers and expandable clays such as smectite are likely to have been damaged. The results presented in Table 2.4 for these wells were measured during the AQUA-DK Project (Springer et al., 2010) on samples taken from core material that was in a very poor condition. The situation is quite different for the Stenlille data. The porosity-permeability data in Table 2.4 were measured within a few weeks after the core had been drilled. However, the samples were cleaned and dried before analysis as is normal practice in routine core analysis (API RP40, 1998), and expandable clays will therefore shrink. This will induce microcracks in the mudstone that will enhance the measured permeability, affect the mercury injection data and therefore cause a misinterpretation of the quality of the caprock. A spectacular demonstration can be seen from the Stenlille-2 sample at 1484.70 m depth (Table 2.4). The porosity and liquid permeability was measured on a preserved (fresh) black shale that was brought to reservoir P and T conditions at ≈ 1500 m depth (Springer et al. 2010). The measured liquid (brine) permeability of 3 nD is in line with the best petroleum caprocks. From the same depth a small sample was cleaned and dried and used for mercury injection test. The result r_{10} shows that 10% of the pore volume of the sample consist of pores with a pore throat radius $\geq$ 600 nm. If this was a true result then the brine permeability would be several orders of magnitude higher than the actual 3 nD measured. The reason for this discrepancy is likely the relatively high content of smectite present in the sample that, when dried, leave microcracks of much larger dimensions than seen for pores in a fresh (wet) sample. Data on entry pressure to CO_2 and super critical (dense) CO_2 was also presented in this study (Table 2.6).

Table 2.4. Petrophysical data for the Fjerritslev Formation obtained from routine core analysis of the listed onshore wells. Observe that the highlighted Stenlille sample at 1484.70 m is the only reservoir condition result available. Permeability is measured on vertically drilled plugs (perpendicular to the bedding in the core) unless otherwise given for a few plugs that are horizontal (postfix H in the table below). Entry pressure and pore throat radius are obtained from standard mercury injection tests on cleaned and dried samples (Springer et al. 2010), cf. details below.

Well ID	**MD [m]**	**Gas permeability [µD]**	**Liquid permeability [µD]**	**Porosity [%]**	**MICP entry $P_{(air\text{-}brine)}$ [MPa]**	**Pore throat radius r_{50} [nm]**	**r_{10}**	**Mean hydraulic radius [µm]**
Børglum-1	1114.54	1980		20.0				
	1115.19	2080		21.7				
	1116.79	4740		18.9				
Farsø-1	1976.69	~ 0		9.1				
Vedsted-1	1403.33	55		14.9				
	1403.40			15.2	6.0	10	38	0.16
	1407.10			17.6	7.5	9	22	0.18
	1865.40			8.3	11.0	5	150	0.51
	1868.23	22		3.0				
	1868.60 **H**	40		10.0	9.5	6	300	0.80
	1869.27	60		12.1				
Stenlille-1	1501.33 **H**	21		13.0				
	1501.33			9.5	6.5	9	200	0.76
Stenlille-2	1484.70 **H**	15		17.0				
	1484.70			13.0	7.5	8	600	2.35
	1484.70		0.003	13.8				
	1493.43 **H**	475		8.9				
Stenlille-4	1493.10 **H**	5040	73	14.6				
	1498.10 **H**		19	13.2				
Stenlille-5	1531.60 **H**	2763		5.3				
Stenlille-6	1544.40 **H**		3219	16.3				
	1550.58	137		9.7				
	1551.53	687		9.5				
	1552.44	305		11.0				
	1553.34	116		10.3				
	1554.45	45		9.4				
	1555.83	69		11.6				
	1556.81	798		8.5				
	1557.67	687		8.4				
	1558.88	857		9.8				
Stenlille-10	1503.20 **H**	138		3.7				
	1503.33	13		1.4				
	1513.29	117		12.0				
	1513.90 **H**	166		11.2				
	1514.33	118		12.6				
	1515.33	44		13.2				
	1516.35	3		11.4				
	1517.33	20		10.5				
	1517.93	309		11.0				

The unit of permeability: Darcy (D) ≈ 10^{-12} (m^2) ; micro Darcy (µD) ≈ 10^{-18} (m^2). Seal capacity data from MICP (Mercury Injection Capillary Pressure): The entry pressure have been recalculated to an air-brine system using standard values for interfacial tension and contact angle; a CO_2-brine system would imply significantly lower figures for the entry pressure. Pore throat radius: r_{10} and r_{50} denotes the pore throat radius in nm (nano meter) where 10% and 50% respectively of the sample pore volume have been filled by injected mercury. The relation between r_{10} and r_{50} denotes a kind of pore throat sorting index but see comments below.

Table 2.5. A summary of results obtained from analysis of cuttings from the Fjerritslev Formation in 3 onshore wells in the Danish Basin. For further details refer to Mbia et al. (2014), Table 1. Helium (He) and mercury (Hg) porosity is given as an average of between 4 and 10 cuttings samples taken from each well. Results from analysis of a few natural state core plugs are also given in the table below. k_{BET} is a permeability calculated from Kozeny's equation and measured specific surface area by the BET method. k_{CRS} is a measured overburden liquid permeability from a constant rate of strain (CRS) experiment.

Well ID	Depth interval	He-porosity	Hg-porosity	NMR-porosity	Permeability	Plug permeability *	
	MD [m]	Avg. [%]	Avg. [%]	[%]	k_{BET} [µD]	k_{BET} [µD]	k_{CRS} [µD]
Vedsted-1	1585-2005	22	nd	nd	0.6	nd	nd
Stenlille-2	1475-1486	20	10	21*	0.2	0.2	0.2
Stenlille-5	1419-1576	21	11	18*	0.35	0.2	nd

* Measured on a few preserved (natural state) core plugs.

Table 2.6. Reservoir condition (rescon) data measured for the Fjerritslev Formation mudstone caprock from the Stenlille-2 well, i.e. at 50 °C and 168 bar effective confining stress (Springer et al. 2010). Besides the liquid permeability, data are given for nitrogen (N_2) and carbon dioxide (CO_2) in gas and super critical condition.

Sample	Liq. perm @ rescon		N_2		gasCO_2		scCO_2	
ID	[nD]		Pce [bar]	P_{BT}	Pce [bar]	P_{BT}	Pce [bar]	P_{BT}
St-2/1A	2.6 *	~ 3 *	80	80	70	nd	50	60

Legend: P_{ce} *– capillary entry pressure*

P_{BT} *– Break Through pressure*

** the liquid permeability is determined from 2 independent instruments*

In the light of missing core material from the Fjerritslev Formation in most wells, the study on cuttings by Mbia et al. (2014) is encouraging and convincingly demonstrates that useful data can be extracted by careful preparation and analysis of old unwashed material left at surface conditions for more than 25 years. As for the RCA data in Table 2.4 it can be argued that 1. the long storage before analysis and 2. the cleaning and drying caused "chemical weathering/damage to the sample" that may have affected (tend to increase) the porosity and permeability results. The cuttings study also demonstrated that different analytical methods yield different results for mudstones; the significant low Hg-porosity figures in Table 2.5 though is a well-known phenomenon in tight rocks, and due to Hg not entering the small pore throats with $r \leq 2$ nm during the high pressure cycle of the injection.

In summary, the measured dry gas permeabilities from RCA measurements (Table 2.4) grossly overestimates the true permeability of an undamaged caprock. Besides the liquid (brine) permeability is more relevant for an aquifer storage, and is expected to be orders of magnitude lower than the measured gas permeabilities as demonstrated for the Stenlille reservoir condition measurements in Table 2.5 and 2.6. Smectite-rich shales will yield false dual porosity pore networks when subjected to MICP tests, and the capillary entry pressure data estimated from such tests may be affected and difficult to interpret correctly (Krushin, 1997).

2.7. Future caprock work

Future research on the Fjerritslev Formation caprock should focus on several tracks:

1. Potential CCS sites will be drilled before a storage operation is initiated, and core in both the caprock and the reservoir should be cut. An advanced laboratory caprock study (eg. Springer *et al.* 2010) should be executed as soon as possible after the core has been cut in order to avoid damage to the samples. Likewise, advanced rock mechanics study on fresh samples should be carried out immediately after the core has been cut.

2. Existing core material fall in two categories, a) Preserved core that remain in a preserved state after many years, and b) Dry core material that was cleaned soon after the core was cut and still remain in GEUS core store; this will typically be as plug samples that have been analysed in previous studies without having been damaged.

With respect to 2a) preserved caprock core is only available from the Stenlille wells and can as such be used for advanced testing like any freshly cut core. With respect to 2b) the study by Mbia et al. (2014) has demonstrated (with some reservations) that uncleaned cuttings can be brought to a restored state by careful handling. Thus old wells near potential CO_2 sequestration sites may still give useful petrophysical data until new wells are decided for.

3. The mineralogical variations of the Fjerritslev Formation are important to understand to estimate the possible CO_2 interaction with the caprock and because some minerals such as smectite can swell during drilling of a well which may compromise the operation. Thus, is it recommended to analyze the clay mineralogy of many samples to unravel the variation in lateral distribution related to source area and basin dynamics as well as the effect of burial on diagenesis. Core material of the Fjerritslev Formation exists from several Danish onshore wells of which few have been applied for clay mineral analysis and with varying interpretation procedures. The clay mineral analyses of core pieces may be supplemented by analyses of cuttings material which has shown to give valuable information. Petrographic examination of the clay minerals is also recommended to estimate the proportion of detrital versus authigenic minerals.

4. The lithological heterogeneity in the Fjerritslev Formation pose a risk to the seal capacity as silty and sandy layers may compromise the seal efficiency if they are too abundant for the seal to be sufficiently tight. De-risking of this would require detailed Palaeogeographical maps and understanding of source areas. For the latter part provenance analysis is recommended to determine the source areas for the silt and sand particles and thereby to help evaluate their distribution in the basin. This can be achieved by radiometric age dating such as U/Pb analysis of zircon grains similarly to results obtained from the Gassum Formation, which revealed that sediment was supplied to the basin from several directions hence explaining the variations found in sandstone thickness and mineralogical composition. If several source areas contributed sediment to the basin during deposition of the Fjerritslev Formation, this may have caused lateral variations in the clay mineral assemblage that are important to recognize.

2.8. Rock type variations in the Fjerritslev Formation

Wire-line logs provide important indirect information to assist in the caprock analysis. The analysis include rock classification (typing) and calculation of properties that like all other indirect analysis should be integrated with direct measurements obtained on core material.

Table 2.7. Rock type classification in the Stenlille area and its wire-line rock signature.

		Wireline log					Calculated		
Formation	**Rock type**	**GR**	**Density**	**Resistivity**	**N-PHI**	**Sonic**	**UCS**	**Porosity**	**Permeability**
Gassum	Sandy	low	low	low	medium	medium	medium	high	high
Gassum	Shaly	high	high	high	high	high	high	medium	low
Gassum	Coal	low	low	high	high	low	low	low	low
Fjerritslev	Seal	high	high	high	high	low	low	low	none
Fjerritslev	Muddy	high	high	high	medium	medium	medium	medium	low
Fjerritslev	Sandy	low	medium	low	medium	high	high	high	low

Currently, no regional caprock or intra-seal evaluation of the Fjerritslev and Gassum formations has been published and thus available for this review. In order to illustrate some of the features that such study may add we here report on a preliminary study made on the Stenlille-2 well (Schovsbo et al., in preparation). In this study the normally available suite of wire-line logs such as the gamma ray log (natural radioactivity), neutron porosity, formation resistivity and modelled parameters such as unconfined compressional strength (from sonic P-wave i.e. Awang et al., 2017), porosity and permeability (from wire-line core analysis i.e. Esbensen et al., 2015) was used to define the rock types (Table 2.7, Figure 2.3).

In defining the rock types from wire-line logs the following characteristics have been applied; claystone, siltstone, sandstone and coal (Table 2.7). It should be noted that grain sizes cannot be deducted from the wire-line logs as these respond to mineral composition and texture and fluid concentration and type. The mudstone and siltstone are here fine-grained rock with either above 50% clay or below 50% clay respectfully. The clay is laminar to dispersed. Sandstone is a coarse-grained quartz rich and low clay (<25%) rock with structural to pore filling clay.

In the Fjerritslev Formation:
The claystone rock type is defined as rock with highest clay content characterised by high natural gamma, high neutron porosity, high formation resistivity, low porosity and no modelled permeabilities.
The siltstone rock type is defined as rock with medium clay content characterised as above but with medium neuron porosities, sonic velocities and porosities
The sandstone rock type is defined as having low clay content and is characterised by low GR, neutron porosities and high porosities.

In the Gassum Formation:
The sandstone rock type is characterised by low gamma ray, high porosity and high to medium permeabilities.
The siltstone rock type may include coal seams and is characterised by medium to high gamma rays and medium porosities and low permeabilities.

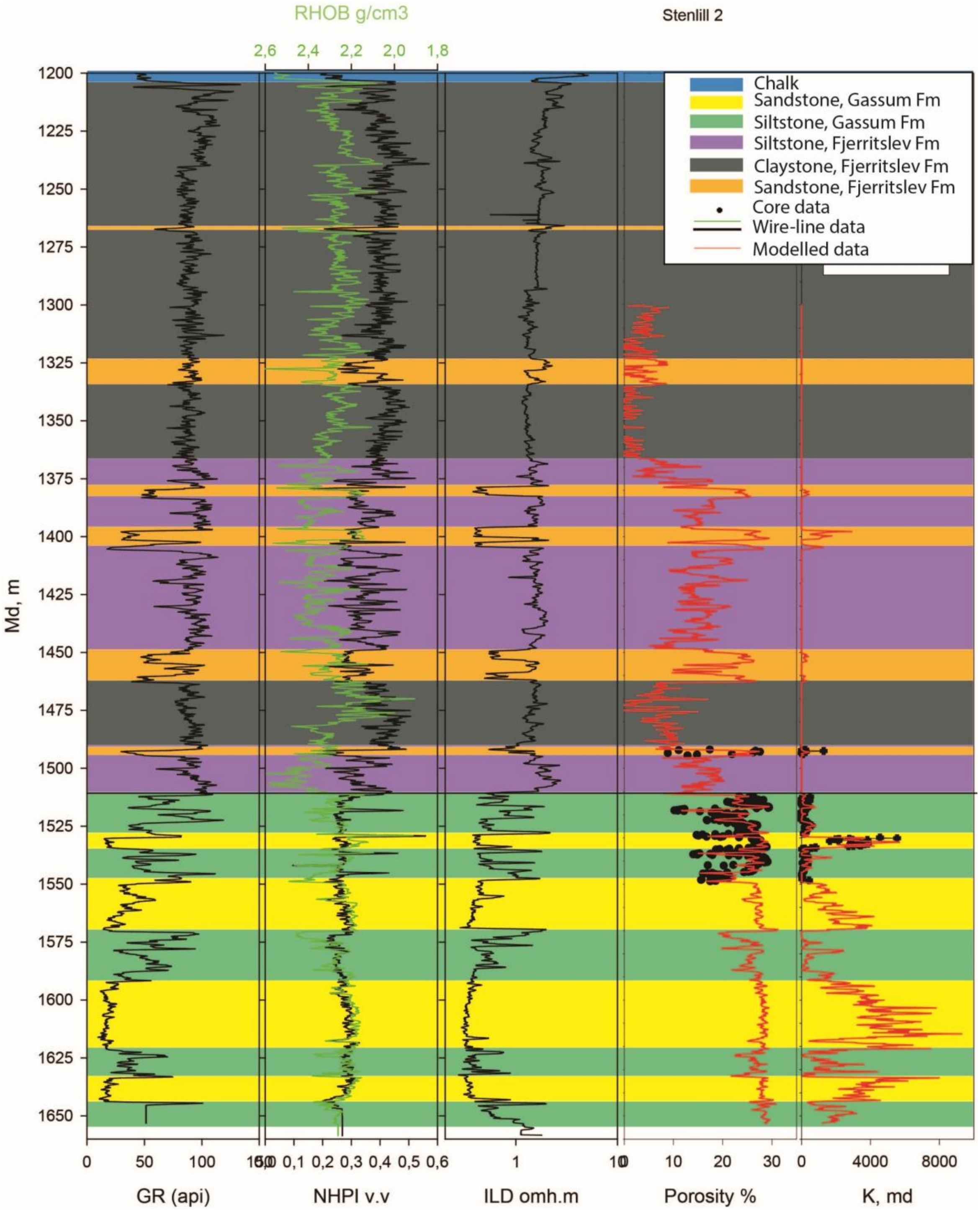


Figure 2.3. Example of well log analysis from the Stenlille-2. Porosities and permeabilities (K) are calculated from wire-line logs based on a partial least square regression model (PLS-r, c.f. Esbensen et al., 2015) established on core data (Schovsbo et al., in preparation). Porosity and permeability predicted in the Fjerritslev Formation is only indicative and awaits validation with core measurements.

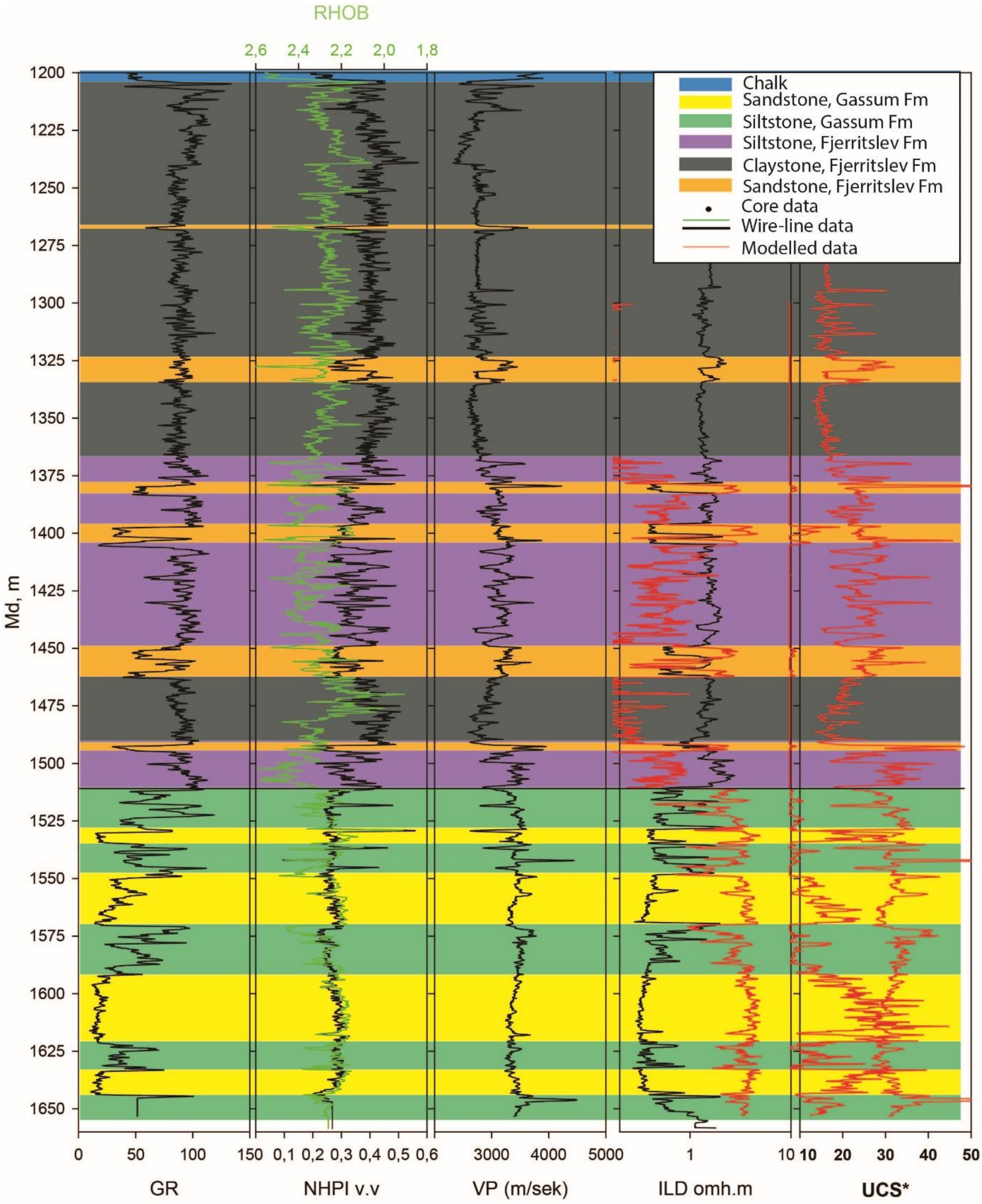


Figure 2.3 (Continued). - Example of well log analysis from Stenlille-2. UCS* (Unconfined compressional strength in MPa) is calculated from sonic log P-velocity assuming a fixed Vp/Vs ratio and should only be used as indicative of high versus low rock strength.

Both the claystone and siltstone have seal properties with the highest capacity within the claystone rock type. In the Fjerritslev Formation the claystone has a cumulated thickness of more than 150 m and occur in 5 beds separated by sandstone or siltstone beds. In the Gassum Formation 4 up to 20 m thick siltstone beds occur separating porous sandstone. The siltstone beds correspond to offshore and lagoon mudstone facies but also include a few thin beds of shore face sand according to the description of Stenlille-2 in Hamberg and Nielsen (2000). The sandstone rock type corresponds to shore face sand and back barrier sand according to the same authors.

In the Stenlille gas storage the siltstone rock type act as an intra formational seal for gas stored in the sands, eg. Høier and Springer (2001). It is likely that the seal is not sustained over geological times albeit it may possess a barrier for flow within an operational context. It is thus expected that such beds may also act as a barrier for CO_2 filling operations as observed eg. in the Utsira Sand reservoir where sequestration of separated CO_2 from the Sleipner Field has taken place since 1998 (Arts et al., 2008).

2.9. Formation water chemistry

Although almost one hundred deep (> 500 m) wells have been drilled on-shore Denmark, reliable formation water chemistry data were only obtained from relatively few of these wells. Until 1978, wells were mostly drilled for oil exploration purposes, and only few tests were performed since no commercial quantities of oil had been encountered. After 1978, drilling activities relating to geothermal energy, natural gas underground storage and nuclear high-level waste storage planning greatly enhanced our knowledge on formation water chemistry. An overview of existing knowledge of formation water chemistry of Danish saline formation waters is given in Laier (2008). The formation water chemistry of the Fjerritslev Formation is only measured in a single well as shown in Figure 2.4 and Table 2.8 and thus the formation water chemistry of the Fjerritslev Formation above the Hanstholm and Havnsø structures is fairly undefined.

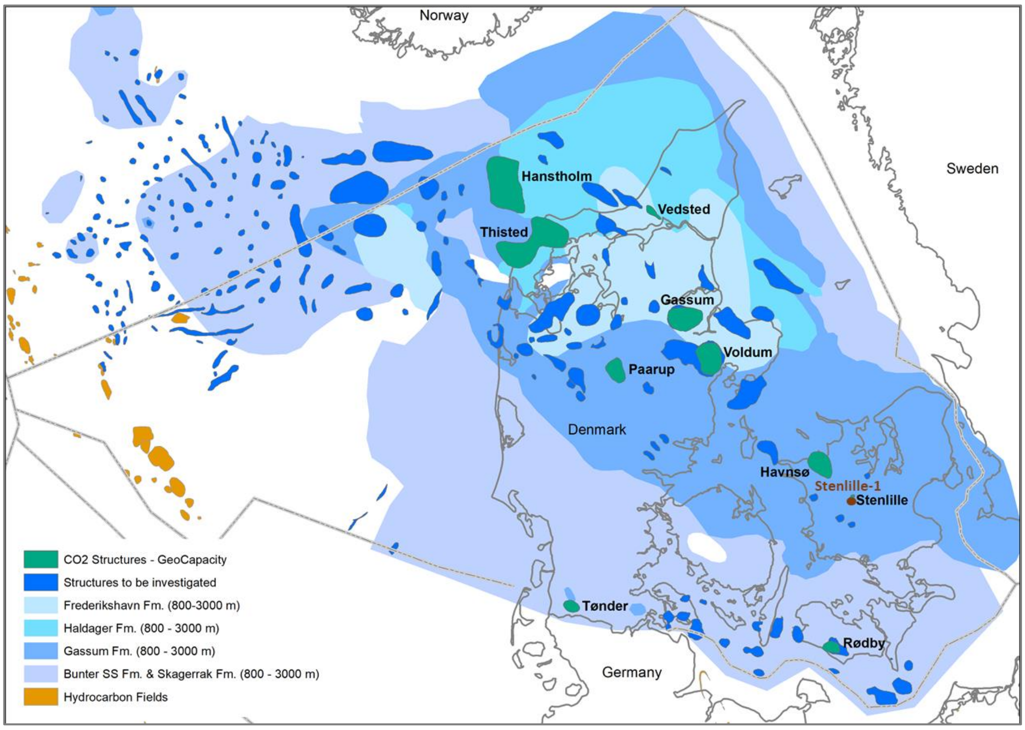


Figure 2.4 Location of wells in which the formation water chemistry of the Fjerritslev formation is known (Laier, 2008). For comparison also the location of the Hanstholm and Havnsø structure is included (From Anthonsen et al., 2011).

Table 2.8 Formation water chemistry of the Fjerritslev Formation in the Stenlille-1 well (Laier, 2008)

Formation		Fjerritslev
Well		Stenlille-1
Depth	m	1370
pH		6.4
Cl	g/L	103
SO_4^{2-}	g/L	0.015
Br	g/L	0.31
HCO_3^-	g/L	0.061
Na	g/L	58
Ca	g/L	5.7
Mg	g/L	1.4
K	g/L	0.29
Sr	g/L	0.6
Fe	g/L	0.03
NH_4	mg/L	59
Ba	mg/L	60
Zn	mg/L	0.8
Li	mg/L	0.9
SiO_2	mg/L	6
I	mg/L	13

3. CO_2 – caprock interaction

In principle, pure and dry CO_2 is not reactive towards rocks, but in aqueous solution a portion of the CO_2 will, depending on temperature and pressure, react with water (H_2O) to form carbonic acid (H_2CO_3). Thus, CO_2 and H_2O are mutually soluble. It is the formation of carbonic acid and the concomitant decrease in pH that is the main trigger for possible hydrogeochemical reactions between CO_2 and rock forming minerals (Kampmann et al., 2014; Aminu et al., 2017; Rackley, 2017). However, in the case of caprocks, it has been suggested that the presence of dry supercritical CO_2 ($scCO_2$) may also interact physico-chemically with the caprock, and thereby cause changes in the caprock properties (Rempel et al., 2009; Kim et al., 2012; Kampmann et al., 2014).

The major effects mentioned in association with possible CO_2-caprock hydrogeochemical reactions are:

- The CO_2 dissolved in formation water may cause dissolution of rock forming minerals, and thereby may corrode caprocks or fault seals, allowing CO_2 to migrate upwards and caprocks to become geomechanically unstable.
- Precipitation of carbonates in fractures and faults may generate stresses due to the force of crystallization – and thereby create new pathways for upwards migration of CO_2.
- Precipitation of carbonates in fractures and faults enhances the caprock properties due to blocking of possible migration pathways.
- Dry $scCO_2$ may enter fractures and cause shrinking of water-bearing clay minerals such as smectites, thereby facilitating fracture creation and upward migration of CO_2.
- Dry $scCO_2$ may act as solvent for e.g. organic matter and trace elements, thereby enabling upward migration of contaminants to overlying freshwater aquifers.

In order to be important in terms of quantity, these effects all require that CO_2 migrates into the caprock. In a caprock without fractures, the main transport mechanism will be diffusion since the properties that defines the caprock, such as high capillary entry pressure and low permeability, should prevent vertical advective transport of CO_2 at the reservoir-caprock interface. If fractures/faults exist in the caprock at this interface - or are created as a result of the storage operation - there is a possibility that advective transport may take place in such fractures. In general, the present literature suggests that possible migration distances may vary from a few centimeters and up to tens of meters during a period of e.g. hundred thousand years (Gaus, 2010; Shukla et al., 2010; Aminu et al., 2017).

3.1. Possible chemical reactions caused by dry $scCO_2$ in the caprock

The reactions between dry supercritical CO_2 ($scCO_2$) and rock forming minerals have not been studied extensively (Kampmann et al., 2014). However, some studies have dealt with the effects of interaction between dry $scCO_2$ and caprocks. Both mobilization of trace metals (Rempel et al., 2011) and carbonation (Regnault et al., 2009) by dry $scCO_2$ have been suggested, but the mechanisms and rates of these reactions are not well known (e.g. Lin et al., 2008; Lea et al., 2011). Further, the magnitude of such reactions seems limited compared to reactions caused by CO_2 dissolved in brine (Kampmann et al., 2014).

Interaction of dry $scCO_2$ with mineral surfaces may also result in “drying out” and subsequent shrinkage of the caprock clays, thereby enabling new or enhancing existing migration pathways (Rochelle et al., 2004; Kim et al., 2012). This is especially considered to be a possible challenge in the case where caprocks have a high content of swelling clays such as smectites. Since water solubility in CO_2 is relatively low, the process is only considered to be relevant where constant supply of “fresh” dry $scCO_2$ is possible e.g. along fractures and faults (Gaus, 2010).

The magnitude and relevance of chemical reactions between dry $scCO_2$ and caprocks are still not understood fully and are further dependent on local mineralogical variations of the caprock.

3.2. Chemical reactions induced by CO_2 dissolved in brine

Several experimental studies as well as evidence from natural analogues have demonstrated that the corrosive environment caused by dissolution of CO_2 in the formation brine will induce dissolution of rock forming minerals (e.g. Johnson et al., 2004; Rochelle et al., 2004; May, 2005; Liu et al., 2012). Most relevant to caprocks are the dissolution of carbonates, readily reactive silicates such as K-feldspars, and clay minerals. The dominant reactions, the magnitude of dissolution, and possible coupled hydrogeochemical processes such as precipitation of secondary reaction products are dependent on several factors such as the mineral composition of the caprock and the transport of CO_2-containing brine to the caprock.

One of the simplest chemical reactions that may take place is the dissolution of calcite (Appelo and Postma, 2005):

$$CaCO_3 + CO_2 + H_2O <-> Ca^{2+} + 2HCO_3^- \qquad (3.1)$$

Similarly, other carbonates such as siderite and ankerite may readily dissolve if present in the caprock.

Most often more complex reactions are also likely to take place. An example of such a reaction is the reported reaction for the caprock at the Norwegian Sleipner CO_2 storage site where K-feldspar and Mg-chlorite are weathered by CO_2, resulting in the formation of kaolinite, magnesite, muscovite, and chalcedony (Johnson et al., 2004):

$$\begin{aligned} &KAlSi_3O_8 + 2.5Mg_5Al_2Si_3O_{10}(OH)_8 + 12.5CO_2 <-> \\ &\qquad 2KAl_3Si_3O_{10}(OH)_2 + 12.5MgCO_3 + 1.5Al_2Si_2O_5(OH)_4 + 4.5SiO_2 + 6H_2O \qquad (3.2) \end{aligned}$$

If the caprock is free from fractures, the main reactions take place at the reservoir/caprock interface and migration of the reaction front into the caprock is determined by the coupled effect of reaction rates, mineral availability and CO_2 diffusion into the caprock (e.g. Gaus, 2010). If fractures are present, also the supply of CO_2 by advection in the fractures is relevant.

Overall, the CO_2-brine-caprock system constitutes a complex multivariate system where possible hydrogeochemical reactions are dependent on local conditions. The understanding of such systems requires application of site-specific experimental studies and numerical models to predict possible future effects and to quantify uncertainties related to such predicted effects. However, some general conclusions may be drawn from the current state-of-the-art knowledge:

- Most studies point at carbonates as being the most reactive minerals. Dissolution of these may cause increased porosity and enhanced permeability – and as such challenge the caprock properties of the caprock - since the general assumption is that the reaction does not result in precipitation of secondary minerals (cf. Equation 3.1). The overall effect on caprock properties depends amongst others on how far into the caprock, the reaction front will migrate. As mentioned previously, this is determined by the transport process (fracture flow or diffusion) and the abundance of carbonates in the caprock. The general assumption is that during the lifetime of a CO_2 storage project, the migration distance will only be a fraction of the caprock thickness and as such do not pose a risk to the safety of a storage project (e.g. Lindeberg and Bergmo, 2002 and Gaus, 2010). Evaluation of this general assumption is, however, recommended for specific storage projects.

- In addition, dissolution of carbonates may weaken the geomechanical stability of the caprock and cause increased fracture intensity (e.g. Gaus, 2010; Shukla et al., 2010) However, it has been suggested that the pressure relief that is caused by increased fracture intensity will result in degassing of CO_2 along the flowpath of fractures and as a result may cause precipitation of fresh carbonates and closure of fractures. This will, to some degree, ensure the preservation of caprock properties and would likely also be the case if fractures are initially caused by other reasons than chemical reaction e.g. from overpressurization of the caprock (e.g. Shukla et al., 2010; Aminu et al., 2017; Rackley, 2017).
- Next to carbonates, chemical reactions involving reactive clay minerals and silicates such as K-feldspar and chlorite may be important to consider. In general, the dissolution of such minerals will cause secondary precipitation of other minerals such as carbonates and kaolinite (e.g. reaction 3.2). Consequently, such reactions are also expected to have minor effects on the caprock properties (e.g. Gaus, 2010; Rackley 2017).
- Other minerals, such as Fe-oxides, may also dissolve, but the effects on caprock properties are currently not well understood (Kharaka et al., 2006; Kampman et al., 2009)
- Impurities in the CO_2 stream such as H_2S are likely to enhance chemical dissolution reactions described above (e.g. Gaus, 2010).

3.3. Geochemical modelling of $scCO_2$ invasion into the cap rock

Given that several geochemical processes may affect the trapping capability of the seal and that they are related to transport, reactive transport modelling have been broadly applied to understand the temporal evolution of the caprock as geochemical reactions unfold (for reviews, see Jayasekara et al., 2020). The studies have been based on continuum modelling (i.e. a macroscopic description) and many have simulated both fluid flow and geochemical reactions. Initial modelling included only calculation of diffusion rates of CO_2 in the caprock (Lindeberg and Bergmo, 2002). Later modelling expanded the scope with a focus on mainly mineral dissolution and precipitation reactions and the effect they have on i) reestablishing seal integrity after geomechanically widening of microfractures (Johnson et al., 2005) or fracture opening (Gheradi et al., 2007); ii) caprock porosity (Audigane et al., 2007), including the change in water content (Gaus et al., 2005), and the effect of caprock inhomogeneities on the process (Tian et al., 2014; Tian et al., 2019). Finally, clay swelling and its effect on fracture closure has also been modelled (Wang and Peng, 2014).

The studies have shown that much can be learned from geochemical modelling of the caprock. For storage in Denmark, it would be sensible to conduct such modelling to 1) estimate if reactions increase or decrease porosity with time and 2) assess the response of the caprock to invasion of $scCO_2$ to probe if sealing or expansion of pressure induced fractures occur. Here, as an example we will conduct preliminary modelling of the second aspect to increase our understanding of how clay minerals of the Fjerritslev formation might respond to the presence of supercritical CO_2.

The response of the caprock depends in part on the reactivity of clay minerals. Based on the mineralogical analyses of the bottom portion of the Fjerritslev Formation at Stenlille, we can expect the rock to contain approximately 10% smectite. Similar to other phyllosilicates, smectites are composed of sheets of octahedrally (O) and tetrahedrally (T) coordinated cations, that are stacked along the crystallographic c-axis. In smectite, these sheets are assembled in layers in the order T-O-T, with the apices of the tetrahedra oriented towards the octahedral layer (Fig. 3.1). The tetrahedral layers typically contain Si, but substitution may occur with Al and other trivalent metals. For the octahedral layer, extensive substitution can occur between divalent and trivalent cations. The substitution confers the layer with a net negative charge. To compensate for the negative charge of the layers, interlayers exist with loosely held mono- and divalent cations that are variably hydrated. Because the interlayer cations are weakly bonded, they can exchange with cations in solution (cation exchange capacity). Taking exchange of Na^+ for Ca^{2+} as an example and ignoring water, the reaction is:

$$2\ XNa + Ca^{2+}_{(aq)} = 2XCa + 2\ Na^{+}_{(aq)} \qquad (3.3)$$

Here, XNa represents an interlayer Na atom, compensating for a single negative charge in the T-O-T layer (X); 2XCa represents 1 interlayer Ca atom, compensating for 2 negative charges (2X); and $Ca^{2+}_{(aq)}$ and $Na^{+}_{(aq)}$, aqueous Ca and Na.

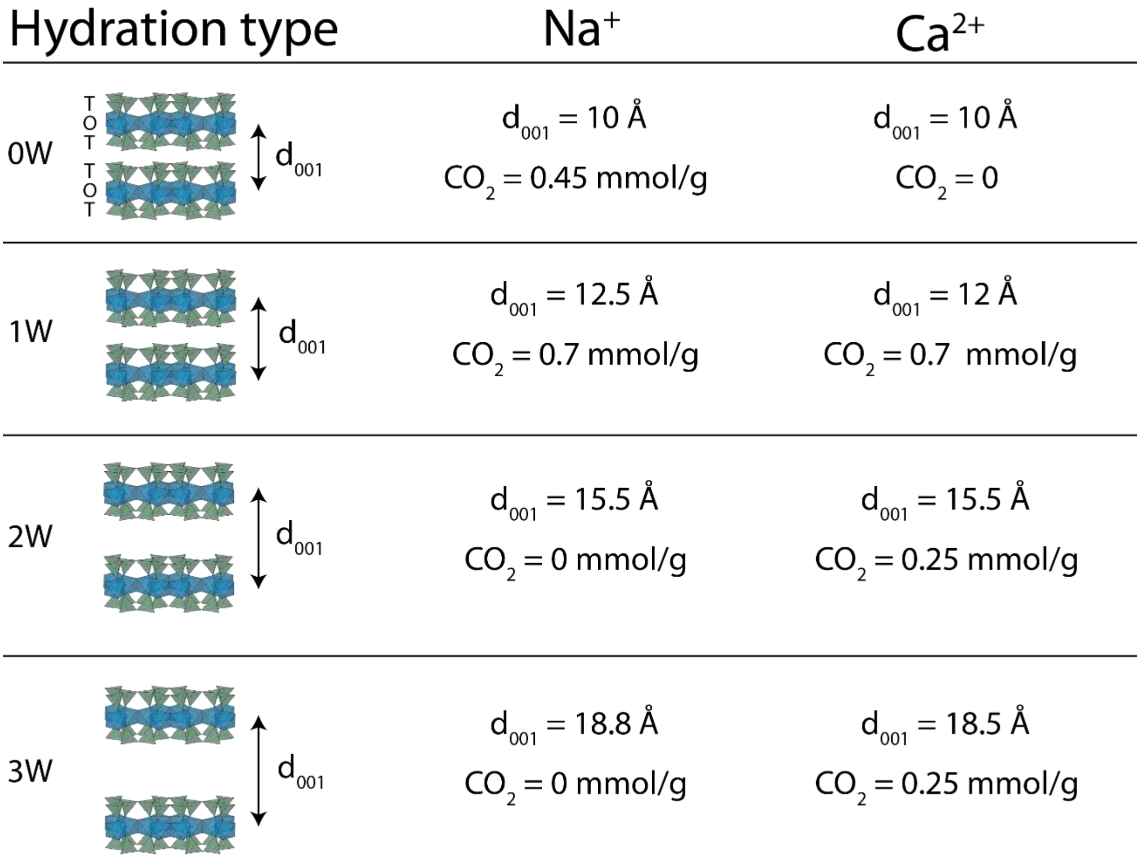


Figure 3.1. Overview of the smectite structure, the hydration types, basal plane distance (d_{001}) and CO_2 uptake. Based on data from Schaef et al. (2015) and Loring et al. (2014). The d_{001} spacing for 0W state is assumed to be identical for both interlayer ions based on values computed with molecular dynamics in Dazas et al. (2014).

The degree of interlayer hydration depends on many parameters, such as the identity of the cation, the charge and its distribution in the T-O-T layer, water activity and temperature (e.g., van Gross and Guggenheim, 1986; Slade et al., 1991; Laird et al., 1996; Dazas et al., 2014; Teich-McGoldrick et al., 2015). Hydration and dehydration of the interlayer cations cause the interlayer distance to change. Typically, such changes are given as modification in the distance between layers along the crystallographic c-axis (basal plane distance; d_{001}), which is readily obtained from X-ray diffraction. The smectite dehydration give rise to distinctive layer distances between basal planes, which corresponds to interlayer hydration states (albeit the nature of the hydration states is debated). With decreasing interlayer hydration and basal plane distance, the hydration states are named 3W, 2W, 1W, and 0W. The (de)hydration reactions involve water. Using a Na saturated smectite as an example, the reaction for hydration of the 0W state is:

$$XNa + Y\ H_2O = XNa(H_2O)_Y \qquad (3.4)$$

where XNa represents the 0W hydration state; Y, the stoichiometry of water transferred to the interlayer; and $XNa(H_2O)_y$, the 1W state. Because water is part of the reaction, the stability of the hydration states depends on the activity of H_2O. The activity of water decreases with increasing concentration of ions and also with increasing dissolution of CO_2, albeit only slightly (~0.02 for CO_2 pressure of 150 bar). Thus, the mere presence of high concentrations of dissolved CO_2 can cause some dehydration of smectite because of its effect on water activity. Depending on the identity of the interlayer cation, some of the hydration states allow considerable uptake of CO_2 in the interlayer. Figure 3.1 provides the value for basal plane distances and rough values for CO_2 uptake for the smectite montmorillonite.

Combining all this information, it is clear that the interaction of the caprock with CO_2 can result in volume changes of the rock and in CO_2 absorption, both of which can affect the transport through fractures. This is particularly true if the CO_2 is undersaturated with respect to water, which would cause evaporation of formation water and increase of the water activity in the CO_2. To test what volume changes and CO_2 uptake could be expected for the smectite fraction of the Fjerritslev Formation, PHREEQC calculations was performed of the interlayer speciation (cation exchange and hydration state) as a function of water activity. In the calculations, the main ions Na^+, Ca^{2+} and Cl^- were considered based on the concentrations given in Table 3.1. Because the concentration of ions is very high, the calculations were performed with the Pitzer database (Appelo et al., 2014) The determined interlayer speciation was then used to calculate interlayer distance and CO_2 uptake based on results in Schaef et al. (2015) and Loring et al. (2014) for the smectite montmorillonite.

Table 3.1. Reactions and parameters used in the PHREEQC modelling.

Hydration state	Reaction	Log $k_{298.15}$	DH^0_r (kJ/mol)
0W	$XNa + 0.5Ca^{2+} = XCa_{0.5} + Na^+$	-4.25	
1W	$XNa + 6.5\ H_2O = XNa(H_2O)_{6.5}$	2	-38.1
2W	$XNa + 12.8\ H_2O = XNa(H_2O)_{12.8}$	4.1	-101.9
3W	$XNa + 18\ H_2O = XNa(H_2O)_{18}$	4.4	-168.8
1W	$XCa_{0.5} + 4\ H_2O = XCa_{0.5}(H_2O)_4$	7.3	-13.4
2W	$XCa_{0.5} + 12.9\ H_2O = XCa_{0.5}(H_2O)_{12.9}$	8.7	-84.2
3W	$XCa_{0.5} + 16\ H_2O = XCa_{0.5}(H_2O)_{16}$	9	-156.2

In the calculation, the reaction constants for cation exchange and interlayer hydration at 25 °C were taken from Marty et al. (2020). To correct for temperature, values for the standard enthalpy of reaction (DH^0_r) for the hydration reactions were taken from Vidal and Dubacq (2009) for the smectite saponite. Albeit this is a different type of smectite than montmorillonite, the ΔH^0_r for the various smectite types in Vidal and Dubacq (2009) differs only little. The ΔH^0_r allows reaction constants to be corrected for temperature with the Van't Hoff equation:

$$log\ K_T = \ log\ K_{298.15K} - \frac{\Delta H_r^0}{2.303 * R}\left(\frac{1}{T} - \frac{1}{298.15K}\right) \qquad (3.5)$$

Here, K_T represents the reaction constant at temperature T (K), $K_{298.15}$, the constant at 298.15 K (25 °C) and R, the gas constant (0.008314 kJ mol^{-1} K^{-1}). The values for DH^0_r provides a temperature dependence that is somewhat overestimated (Vidal and Dubacq, 2009). Thus, calculations were performed at 25 °C as well as the 50 °C expected for the formation. The reactions, their constants and the DH^0_r are given in Table 3.1.

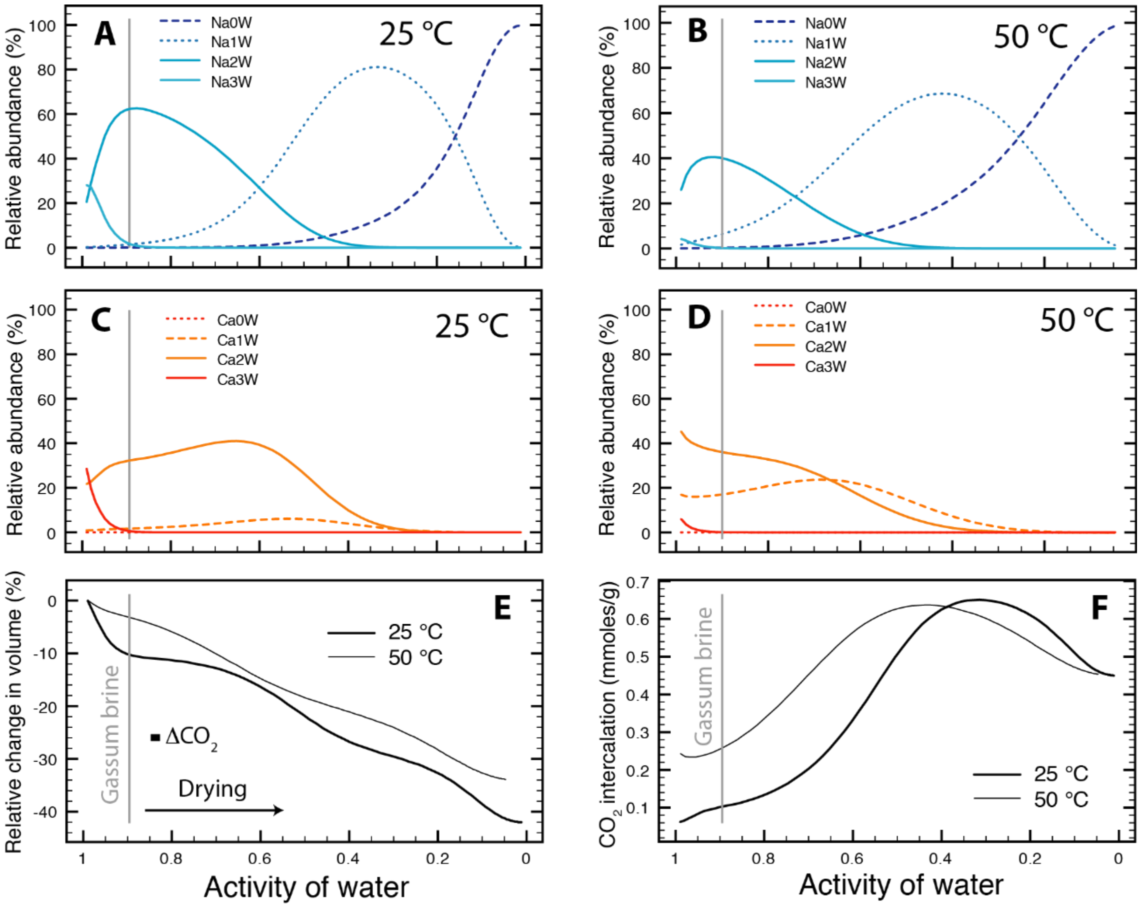


Figure 3.2. Calculated interlayer speciation as a function of the activity of water for Na (A and B) and Ca (C and D) at 25 and 60 °C. The relative change in volume and the CO_2 intercalation as a function of water activity are shown in E and F. The bar indicated by "DCO_2" indicates the change in water activity occurring as a results of CO2 dissolution at 50°C and the water composition of the Fjerritslev brine.

Figure 3.2 shows the results of the calculations for 25 and 50 °C. As expected, the smectite hydration decreases with decreasing water activity for both temperatures. At high to intermediate water activity, the interlayers are approximately equally filled with Na and Ca, but at low water activity, Na dominates. In reality, this trend might be changed because of salt precipitation, which is not included in the calculations. At the water activity calculated for the Gassum brine (indicated by grey lines in Fig. 3.2), the interlayer speciation consists mostly of the partly dehydrated states Na2W and Ca2W. For the 50 °C calculations, the Na1W and Ca1W states also contribute, i.e., the smectite is slightly less hydrated at higher temperature. Because the Na1W and Ca1W states have high affinity for intercalation of CO_2 (Loring et al., 2014; Schaef et al., 2015), the calculated CO_2 uptake capacity is substantial (~0.25 mmol/g smectite). On a volume basis, this is approximately half of the CO_2 uptake by solubility trapping. Given that the volume of pore space and smectite are similar, such uptake would not be without consequences. It could mean that CO_2 intercalation by smectite can provide for retardation of CO_2 passage through the seal, in particular where the fluxes are relatively small such as via diffusion, slow entry into pore space, or through flow in microfractures. The exact effect would have to be calculated with reactive transport calculations.

If supercritical CO_2, that is undersaturated with respect to water (henceforth called subhydrated), reaches the caprock, transfer of water from rock to the supercritical phase would decrease the water activity (indicated by arrow marked "drying" in Fig. 3.2E). This would give rise to dehydration of interlayers (Fig. 3.2A-D). The corresponding volume change would depend on the actual change in the water activity, but the calculations indicate that it could reach ~30%. Given that the smectite accounts for approximately 10% of the volume, the total rock volume could contract by up to 3% which would increase the porosity from ~10% to ~13%. Depending on the location of the clay in the pore spaces and the geomechanical response of the rock, this could cause substantial increase in permeability. Thus, the results of the calculations agree with the arguments presented above to reconcile discrepancies in the permeability measurements; both types of data indicate the unfavorable changes to the caprock that drying may cause.

CO_2 injection may cause the pressure to rise to levels that generate fractures in the caprock. If so, such fractures could conduct upward migration of subhydrated supercritical CO_2. On its way, the supercritical phase would to some extent dry the caprock near the fracture, which could cause the rock to contract. The degree of drying would depend on the flux and hydration of the CO_2, the rate of water transfer from the rock, the water mobility in the rock, and the mineralogical composition of the rock. The actual physical response of the rock would depend on its geomechanical properties. To understand such a dynamic system, more advanced modelling would have to be performed, but we note that the contraction could mean that the fractures widen, which would then increase CO_2 flow and the potential for additional drying. The calculations also indicate that the change in interlayer speciation upon drying would increase the uptake capacity of the smectite (Fig. 3.2F). Whether this could substantially affect the amount of CO_2 passing through the fractures would have to be calculated with reactive transport modelling coupled to fluid transport.

On a final note, the introduction of CO_2 decreases the water activity slightly (bar marked "ΔCO_2" in Fig. 3.2E for the decrease at the water activity of the Gassum brine). For the 50 °C calculations, this causes a change in interlayer speciation that give rise to a volume change of ~0.5 %.

However, the calculations are subject to many uncertainties, including the effect of temperature. Using the results for 25 °C and water activity of about 0.95 as a worst case scenario, the volume change may be ~3%. Because smectite only constitute ~10% of the total rock volume, volume change of 0.5-3 % for the clay may well be inconsequential. For a smectite rich caprock, however, such volume decrease could change the pressure for entry into the pore space. Several studies indicate that mineral-CO_2 interaction facilitates wetting of minerals with CO_2 and eases passage of CO_2 into pore spaces. Mechanistic explanations for the observations include changes in the mineral surface charge (Chiquet et al., 2007) or mineral transformation (Shao et al., 2010). The results of our calculations suggest that the change in water activity from CO_2 dissolution could also facilitate invasion of CO_2 into smectite rich caprock.

Our calculations show how the clay interlayer speciation and dehydration might affect the volume of the caprock. However, a number of parameters control the interlayer speciation, some of which are unknown (e.g., the charge density and distribution in the T-O-T layer of the smectite and their effect on reaction constants) or clearly uncertain (e.g., the brine composition and DH^0_r). In the calculations, we have also omitted the relatively small changes in the basal plane distance of smectites that have been reported to occur upon CO_2 intercalation for the dehydrated hydration states (Giesting et al., 2012a and 2012b). Thus, the results of the calculations merely present one of many possible outcomes of smectite-brine-CO_2 interaction.

Nevertheless, the calculations indicate that substantial volume changes may take place if subhydrated CO_2 leads to drying of the caprock. If the injection scenario is such that subhydrated CO_2 could interact with the caprock, further studies are warranted to substantiate that this would not compromise the integrity of the seal. For the interaction of fully hydrated CO_2 with caprock, the calculated volume change of the smectites is small. Thus, it may not have an effect on the CO_2 mobility. With the available data, we can only perform a crude estimation of the effect. If a fracture exists in the caprock and this conducts supercritical CO_2, diffusion would transport the dissolved species into the caprock. Using a diffusion coefficient of $0.5*10^{-10}$ m^2/s and neglecting uptake by the clay, CO_2 would have migrated to a depth of ~30 cm within a half year and at ~10 cm depth, the CO_2 concentration would be half of that at the caprock/CO_2 interface. (sketch in Fig. 3.3). Taking the ~10 cm depth as a measure of a substantially affected region and assuming that contraction of the caprock is 0.5-3 ‰ for 10% smectite content and occurs equally in all directions, the fracture would widen by approximately 8 to 50 mm. Whether this has bearing on CO_2 mobility, would presumably depend on the initial size of the fractures. Moreover, the volume change may be anisotropic given that clay often settles with its C-axis oriented upwards, meaning that contraction might dominantly take place in the vertical direction, and other volume changing reactions might also operate, such as dissolution and mineral carbonation or expansion of the clays because of CO_2 intercalation.

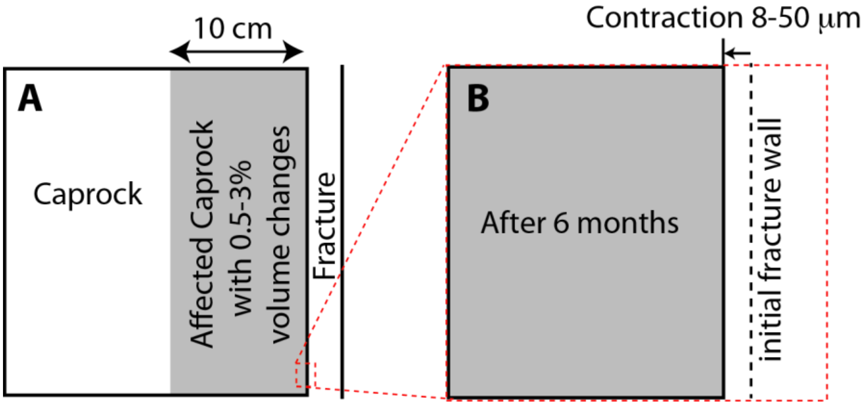


Figure 3.3. A. Sketch of a fracture in caprock and the region of caprock that is assumed to be significantly affected by CO_2. B. Zoom of a region of the fracture-caprock interface showing the original location of the fracture wall and that after interaction with CO_2 and horizontal contraction.

3.4. Experience from Danish caprocks

With regard to possible chemical reactions in Danish caprocks relevant for possible future storage in the Hanstholm and Havnsø structures, only one study has been carried as part of the AQUA-DK project (Kjøller et al., 2010; Weibel et al. 2014). In this study, crushed caprock samples made from stored, dry cores collected at the Stenlille gas storage site were exposed to CO_2 saturated brine at reservoir conditions (70°C; 20 MPa) in a period of up to 14 months. The crushed nature of the samples complicated a thorough petrographical analysis, but the main conclusions from the petrographical study were that (Weibel et al., 2014):

- The Fjerritslev Formation sample contained only small amounts of calcite, dolomite and siderite which did not show clear signs of dissolution as a result of the experiments.
- For the Børglum Formation sample, a caprock occurring in Denmark at a shallower depth than the Fjerritslev Formation, dolomite appeared with clear dissolution features after the experiments.

Based on the experimental results, predictive numerical models were used to explore possible mineral reactions over a period of 1000 years (Kjøller et al., 2010). The models generally suggest that at the interface between caprock and CO_2, assuming that CO_2 supply to this interface is unlimited during storage, it is likely that a variety of coupled mineral reactions will take place even during a period of 50 years. The major reactions for the Fjerritslev Formation are dolomitization of calcite and weathering of illite and Ca-montmorillonite to kaolinite. For the Børglum Formation, the absence of calcite in the formation facilitates carbonization of some of the CO_2, and again weathering of other clay minerals to kaolinite is suggested to take place.

Based on the numerical modelling, rough estimates suggest that the mineral reactions result only in minor changes in total porosity. However, the numerical models are basic conceptual batch models that should be supplemented by site specific models in order to enable evaluation of possible risks associated with mineral reactions in the caprock. Such site specific models may include considerations regarding i) clay contraction caused by drying of the clays ii) transport of CO_2 into the caprock, and iii) geomechanical effects coupled to the mineral reactions.

4. Recommendations for future caprock work

The few data from fresh samples of Danish caprocks clearly demonstrates the need for future studies designed to evaluate possible long-term CO_2-caprock chemical interactions as well as uncertainties associated with predictions regarding possible effects of such interaction. The studies should aim at a cross-disciplinary approach, amongst others including. experimental studies and numerical modelling with focus on both hydrogeochemistry, petrophysics, and geomechanics.

The future site-specific research on the Fjerritslev Formation should focus on new core material of the caprock. Advanced laboratory caprock studies – including petrophysical, rock mechanical and hydrogeochemical studies - should be executed as soon as possible after the core has been cut in order to avoid damages to the samples. We also recommend making advanced pressure testing in the well to establish the rock strength and features such as the fracture propagation pressure.

Although we already have a fair amount of information about the caprock, there are many things we do not know. We recommend that future work on the Fjerritslev Formation caprock occur in three stages to make best use of the information we have and optimise the outcome of the work.

In Stage 1, we will use existing information and available samples to answer critical questions with both experimental and computational techniques:

Stage 1a Computational work. Experimental work is costly and time consuming and the obtained information is specific to the experimental setup and the conditions selected. Hence, it is often most effective if performed when scientific questions can be specific and well posed. Geochemical modelling can help us define the questions, that require experimental answers. In Stage 1a we will conduct detailed petrophysical evaluation of rock types in the evaluable wells to provide a solid framework for subsequent work. Initial reactive transport modelling will be made to identify the overall behavior of the system, the nature and location of critical geochemical reactions, and the parameters that are unknown or highly uncertain. This will allow us to make informed decisions about what experimental work to perform.

The computational modelling for the caprock is highly linked to that conducted for the reservoir, which will provide estimates of the nature and amounts of CO_2 reaching the caprock. The values for many of the input parameters in the modelling are uncertain at this point. Moreover, we wish to identify uncertainties that most critically affect the modelled performance of the CO_2 storage, so that we can constrain the values better experimentally. This means that comprehensive sensitivity analysis will have to be performed. This analysis will be computationally expensive, and we will most likely have to compromise by simplifying other aspects of the model, such as the spatial or temporal resolution or the number of processes modelled simultaneously. This screening by modelling allows us to recognize what types of additional information is required to understand the caprock response to CO_2 and design experiments accordingly. Modelling of key petrophysical parameters such as rock strength, porosity and permeability will form the basis for the analysis.

Stage 1b. Experimental work. We currently assume that the Fjerritslev Formation will perform adequately as a seal for injected CO_2. This assumption is based largely on the advanced laboratory study of a single sample (Springer et al., 2010). Given the importance of the caprock for the safety of the storage, it is crucial to obtain additional high-quality data on its sealing capacity for CO_2. In addition, the amount of clay, the clay mineralogy and the spatial variation should be determined for the Fjerritslev formation so that volume changes can be estimated. Techniques could include X-ray diffraction and electron microscopy coupled with energy dispersive X-ray spectroscopy to determine the mineral structure, abundance, composition and spatial relationship. Finally, advanced rock mechanics studies would be important to gauge the response of the caprock to pressure changes and to volume changes of the clay. This work should be conducted regardless of the results the modelling provides. Prior to detailed site investigation and the drilling operations, we have to rely on existing core material. This material falls in two categories, a). Preserved core that remain in a preserved state after many years, and b). Dry core material that was cleaned soon after the core was cut and still remain in GEUS core store; this will typically be as plug samples that have been analysed in previous studies without having been damaged.

With respect to a) preserved caprock core is only available from the Stenlille wells and can as such be used for advanced testing like any freshly cut core. With respect to b) it should be considered whether old plugs (and possibly cuttings) may be restored and aged in simulated formation water (brine), then pre-consolidated to close microcracks and analysed in an advanced testing programme. Old caprock core that was never cleaned may be used in some caprock tests but is generally not recommended.

In addition to the advanced studies of caprock outlined above, several additional experimental studies could be conducted depending on the outcome of the modelling. These studies could include advanced detailed characterisation of the bulk caprock mineralogy and the clay types. This last study will benefit from experiments using synchrotron radiation. These studies could include X-ray absorption to define the bonding environments of the cations in the T-O-T layers of smectite and quantify the charge distribution, which impact cation exchange and dehydration, and *in situ* X-ray diffraction to determine the response of the smectite interlayers to changes in temperature, the presence of CO_2, and the water activity. Coupling of the results of such studies with the advanced studies of capillary entry pressure would provide unique insight into relationships between geochemical reactions and CO_2 invasion. We estimate that the work in Stage 1 will require 1-2 years.

In Stage 2, we will perform additional advanced laboratory caprock studies. Potential CCS sites will be drilled before a storage operation is initiated, and core in both the caprock and the reservoir should be cut. An advanced laboratory caprock study (eg. Springer et al., 2010) should be executed as soon as possible after the core has been cut in order to avoid damages to the samples. Likewise, advanced rock mechanics study on fresh samples should be carried out immediately after the core has been cut. In addition, we will conduct geochemical experiments directed at answering the specific questions, that the modelling in Stage 1 has raised. Most likely, the work in Stage 2 will require 2 years to complete.

In Stage 3, we will assemble all the information we have obtained in Stage 1 and 2 and during site characterization and conduct elaborate reactive transport modelling to quantify the performance of the caprock during storage. If sufficient information has been obtained from site characterization, this modelling should provide the results outlined by the International Organization for Standardization (ISO 27914:2017), setting the stage for operation. The work will include substantial sensitivity analysis to firmly define uncertainties in the outcomes. We estimate that the Stage 3 modelling can be completed in 1 year.

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