DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2008/48

Chemistry of Danish saline formation waters relevant for core fluid experiments

Fluid chemistry data for lab experiments related to CO_2 storage in deep aquifers

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Abstract

Recommendation concerning the chemistry of the fluids to be used in laboratory tests on core samples from deep geological formations 1000 – 2000 m is presented in this report. The core samples represent formations that are considered possible targets for CO_2 storage in the future. Ideally the fluid initially applied in the laboratory experiments should have a composition similar to that of the original formation waters. However, no formation water samples collected from the formations in question exist at present. Therefore, the experiments need to be performed using synthetic formation water. The information needed for making the correct synthetic formation water may be obtained from available data on formation water chemistry in deep formations onshore Denmark. Unfortunately, fluid chemistry data relevant for only two out of the seven laboratory experiments is available. For the rest of the experiments, extrapolation concerning formation water chemistry has to be made using data from adjacent formations and other wells. Therefore, graphs of formation water composition versus depth have been constructed for all available well data. Fortunately, the trend in formation water chemistry is reasonably well-constrained, allowing for a confident extrapolation of the formation water chemistry data needed. Therefore, it is concluded that the uncertainty with respect to fluid chemistry is not of great importance for the laboratory tests to be performed.

Contents

Abstract

Background

A number of laboratory tests has been planned in order to investigate the mineralogical changes that may occur as a result of CO_2 injection into geological formations. Initial investigations have indicated that a number of sandstone formations of Triassic to Jurassic age may by suitable targets for future CO_2 storage. Therefore, a number of core samples representing these formations have been selected from deep wells drilled previously. The formations and the wells from which the samples have been taken are listed in Table 1.

Table 1. *List of core samples for laboratory tests*

	Formation	Depth, m	Geol. period	Stage	Well
Reservoir	1. Gassum Fm	1662	U Triassic	Raethian	Stenlille-18
Reservoir	2. Gassum Fm	2009	U Triassic	Raethian	Vedsted-1
Reservoir	3. Haldager Sand Fm	1150	M Jurassic	Aalenian-Oxfordian	Vedsted-1
Cap rock	4. Børglum Fm	1041	U Jurassic	Kimmridgian-Volgian	Haldager-1
Cap rock	5. Fjerritslev Fm	1500	L Jurassic	Hettangian-Toarcian	Stenlille-1
Reservoir	6. Bunter Sandstone Fm	1662	L Triassic		Tønder-4
Reservoir	7. Skagerrak Fm (possib.)	2064	M/U Triassic		Vedsted-1

To be able to carry out the water rock interaction experiments in the laboratory formation water samples are needed, either genuine or synthetic. Unfortunately no genuine formation water samples exist at Geological Survey of Denmark and Greenland (GEUS) for any of the wells listed in Table 1. This is so because no tests were performed in the wells listed in Table 1except for Stenlille-1, furthermore the samples recovered from Stenlille-1 in 1980 are no longer available.

Formation water data from well tests

Representative samples of formation water from the Fjerritslev and the Gassum Formations were obtained during the pumping tests of the Stenlille-1 well in 1980, Table 2. The data on formation water chemistry from the two formations, Table 3, may be used directly to make synthetic formation water for the laboratory experiments on core samples from *Stenlille-1* and *Stenlille-18* respectively.

For the other five sets of core samples mentioned in Ttable 1 less precise data regarding formation water chemistry is available. In the *Haldager-1* well four drill stem tests (DST) were performed while in the Vedsted-1 and Tønder-4 no tests were performed. According to the completion report of the Haldager-1 well (drilled in 1950) the chloride content of the water recovered from DST#3 1132-1154 m varied from 68,000 ppm near the top to 130,000 ppm near the bottom of the test. No other data regarding formation water chemistry were given in the completion report. However, water samples from the various tests handed over to Geological Survey of Denmark were analysed in 1960 (Dinesen, 1961). The results of analysis most representative for the formation water of DST#3 is shown in Table 4.

Table 2. *Well tests of deep onshore wells in Denmark*

Well *)	Formation	Depth, m	Test	duration	sampling	Year	Reported
Aars1a	Gassum	3200	airlift	8h	wellhead	1979	DONG 1982
-	Haldager	2485	pumping	3x8d	wellhead	1981	DONG 1982
Farsø 1	Gassum	2840	pumping	20d	wellhead	1982	DGU 1982
Stenlille 1	Fjerritslev	1370	pumping	6d	wellhead	1980	DGU 1981
-	Gassum	1510	pumping	13d	wellhead	1980	DGU 1981
Thisted 2	Skagerrak	1950	pumping	20d	wellhead	1982	DGU 1983
-	Gassum	1257	pumping	12d	wellhead	1983	DGU 1983a
Stenlille 19	Bunter	2475	airlift		wellhead	2001	GEUS 2002
-	Falster	2115	airlift		wellhead	2001	GEUS 2002
-	Gassum	1640	airlift		wellhead	2001	GEUS 2002
MAH-1	Bunter SST	2575	airlift		BHS	2002	GEUS 2002a

*) Well locations shown in Fig. 3.

Table 3. *Formation water chemistry data obtained from deep onshore wells in Denmark*

Well		Aars1a		Farsø 1	Stenlille 1		Thisted 2		Stenlille 19			MAH-1
Formation		Gass.	Hald.	Gass.	Fjer.	Gass.	Skag.	Gass.	Bunter	Falster	Gass.	Bunter
Depth	m	3200	2485	2840	1370	1510	1950	1257	2475	2115	1640	2575
pH		6.0	5.2	5.9	6.4	6.2	6.6	6.4				6.6
Cl	g/L	182	167	172	103	108	166	102	197	182	113	136
SO4	g/L	0.15	0.05	0.13	0.015	0.015	0.29	0.01	0.14	0.22	<0.02	0.24
Br	g/L	1.13	1.08	0.92	0.31	0.47	0.98	0.29	1.39	0.46	0.44	0.87
HCO3	g/L	0.21	0.06	0.128	0.061	0.077	0.03	0.043				0.033
Na	g/L	76	74	73	58	58	70	55	75	96	59	54
Ca	g/L	32.7	23.5	28.00	5.7	8.6	23.5	7.5	40.5	19.5	11.5	23.5
Mg	g/L	2.30	2.95	2.00	1.40	1.64	3.34	1.50	4.00	2.33	1.14	2.91
K	g/L	1.8	0.75	1.6	0.29	0.37	1.88	0.25	3.3	1.7	1.1	0.69
Sr	g/L	0.9	0.7	0.92	0.6	0.64	0.62	0.38	1.01	0.74	0.66	0.91
Fe	g/L	0.6	0.27	0.5	0.03	0.06	0.03	0.04				0.005
NH4	mg/L		105	105	59	60	1.5	52				
Ba	mg/L		50	20	60		5		8.1	4.8	39	5.8
Zn	mg/L		6	37	0.8		16	1	4.4	37	65	7
Li	mg/L		4	13	0.9		14	2	22	15	2.7	12
SiO2	mg/L		48	32	6	16	9	26				
I	mg/L		14	15	13		6					
B	mg/L			40			35					
As	mg/L			<0.1			<0.1					

Comparing the information on formation water chlorinity from the completion report with the analytical data of Table 4 it is obvious that the 130,000 ppm mentioned in the report refer to total salinity and not just to chloride. No information on the chemistry of drilling fluid is given in the reports of the Haldager-1 well, however, it must have been less saline than the formation water as the salinity of the DST fluids increases from top to bottom. The data in Table 4 represent water taken “19 stands off the bottom”. One sample taken just above the tester showed a little higher chloride content (Dinesen, 1961), so the formation water may be a little more saline than has been indicated in Table 4.

Table 4. *Water chemistry from Haldager-1, DST#3 1132-1154 m*

Cl	Br	SO4	Na	Ca	Mg	K
84.2	0.32	0.12	42.6	8.11	1.55	0.24

Concentrations are given in g/L

Formation water data from centrifuge extraction of core samples

Core samples from a number of wells have been used for obtaining information on formation water chemistry. The data obtained compare fairly well with formation water chemistry data of water samples from well tests that followed in some of the wells. Normally a tracer (nitrate) was added to the drilling fluid to be able to calculate the degree of mud infiltration in the cores.

The Upper Bunter SST formation penetrated by the*Tønder-4* well constitute a gas reservoir, the gas being nitrogen (99 per cent) plus traces of other gases. Log interpretation of the previous Tønder-3 well did not quite compare with the core porosity data, which lead to the suspicion, that halite cement might be present in the sandstone reservoir. Special precaution was therefore taken when drilling the Tønder-4 well, furthermore a special core analysis programme including pore water extraction had been decided for this well (Laier and Nielsen, 1989). The pore water chemistry obtained for a number of core samples is shown in Table 5. Corrections for 17 – 50 percent of mud infiltration had to be made to obtain the numbers in Table 5.

Table 5. *Pore water chemistry data from Tønder-4, 1660 m*

Cl	Br	SO4	Na	Ca	Mg	K
200	1.5	0.5	115	9.5	1.9	1.7

Concentrations are given in g/L

The various core analysis data agreed fairly well with the log interpretation of the Upper Bunter SST formation of the Tønder-4 well showing the presence of halite cement at different levels, Fig. 1 (Laier and Nielsen, 1989).

For the core samples representing the three formations in the *Vedsted-1* well we have no direct observations concerning formation water chemistry. Therefore, the formation water chemistry of the three formations has to be deduced from other deep wells, as will be explained below.

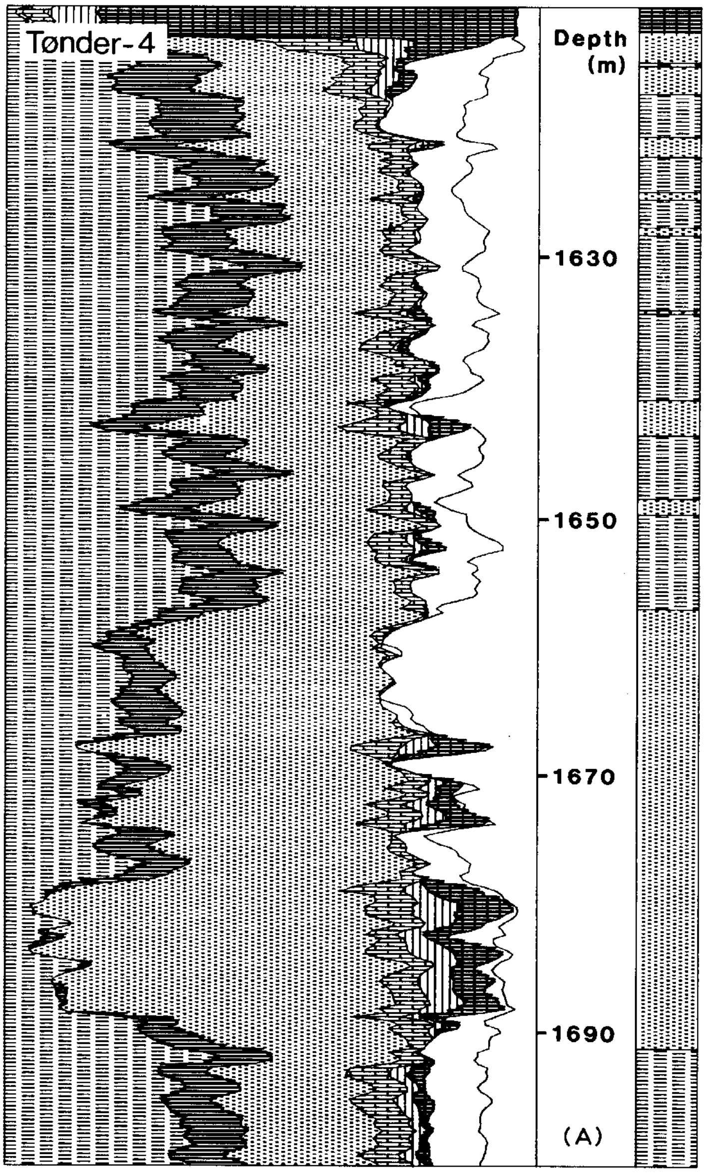

Fig. 1. *Computerized reconstructed lithological log based on density log, γ-ray log, neutron porosity and acoustic log. Lithologies shown from left to right are: shale, hematite, sandstone, limestone, anhydrite, halite, water and gas (N_2).*

Saline formation waters in the Danish Sub basin

Most information on deep formation waters in the Danish Sub basin has been obtained from geothermal exploration wells. However, production tests that provide the most reliable results were only performed in six wells, Tables 2 and 3. Therefore, also formation water from air-lift tests and water obtained from centrifuge extraction of core samples have been analysed to extend the data base on formation water chemistry. The results of the latter samples do not provide information on volatiles (gases) of the formation fluid and concentrations of minor constituents cannot be considered reliable. However, data on major ions is considered to be representative for the formation waters and have been included in the plots of formation water chemistry versus depth, Fig. 2. The well locations relevant for the formation water plots are shown in Fig. 3.

The salinity of formation waters increases gradually with depth approaching saturation with respect to halite (sodium chloride) at approximately 3000 m (Fig. 2A). Close to salt diapirs salinity gradients are steeper with respect to depth as is seen for the Erslev and Tønder wells (Fig. 2A and Fig. 3). The gradual increase in formation water salinity with depth is probably due to diffusion of salt from the large Zechstein salt deposits present in large parts of the basin (Fig. 3). Although increase in salinity due to hyper-filtration through semi-permeable geological clay membranes, may also play a role. Triassic evaporites are also present in some areas. The relatively high bromide to chloride ratios of most formation waters indicate that dissolution of salt is not the primary source, since halite has a lower bromide to chloride ratio compared to sea water (Fig. 2B). The source is more likely the residual brines after the precipitation of the Zechstein salts. Such brines have been encountered in some cases (Dinesen, 1961).

Calcium increases relative to chloride with depth (Fig. 2C). This is probably due to the diagenesis of plagioclase, whereby anorthite is transformed into albite (eq. 1).

$$CaAl_2Si_2O_8 + 2Na^+ + 4SiO_2 \rightarrow 2NaAlSi_3O_8 + Ca^{++} \qquad (1)$$

The degree of diagenesis depends on both temperature and time, and this could explain why calcium concentration increases relative to salinity with depth since temperature of the formation increases with depth.

The calcium to magnesium ratio increases generally with depth, primarily because of the diagenetic reaction mentioned, but also because of dolomitisation of calcite which decreases the magnesium concentration relative to salinity (Fig. 1D).

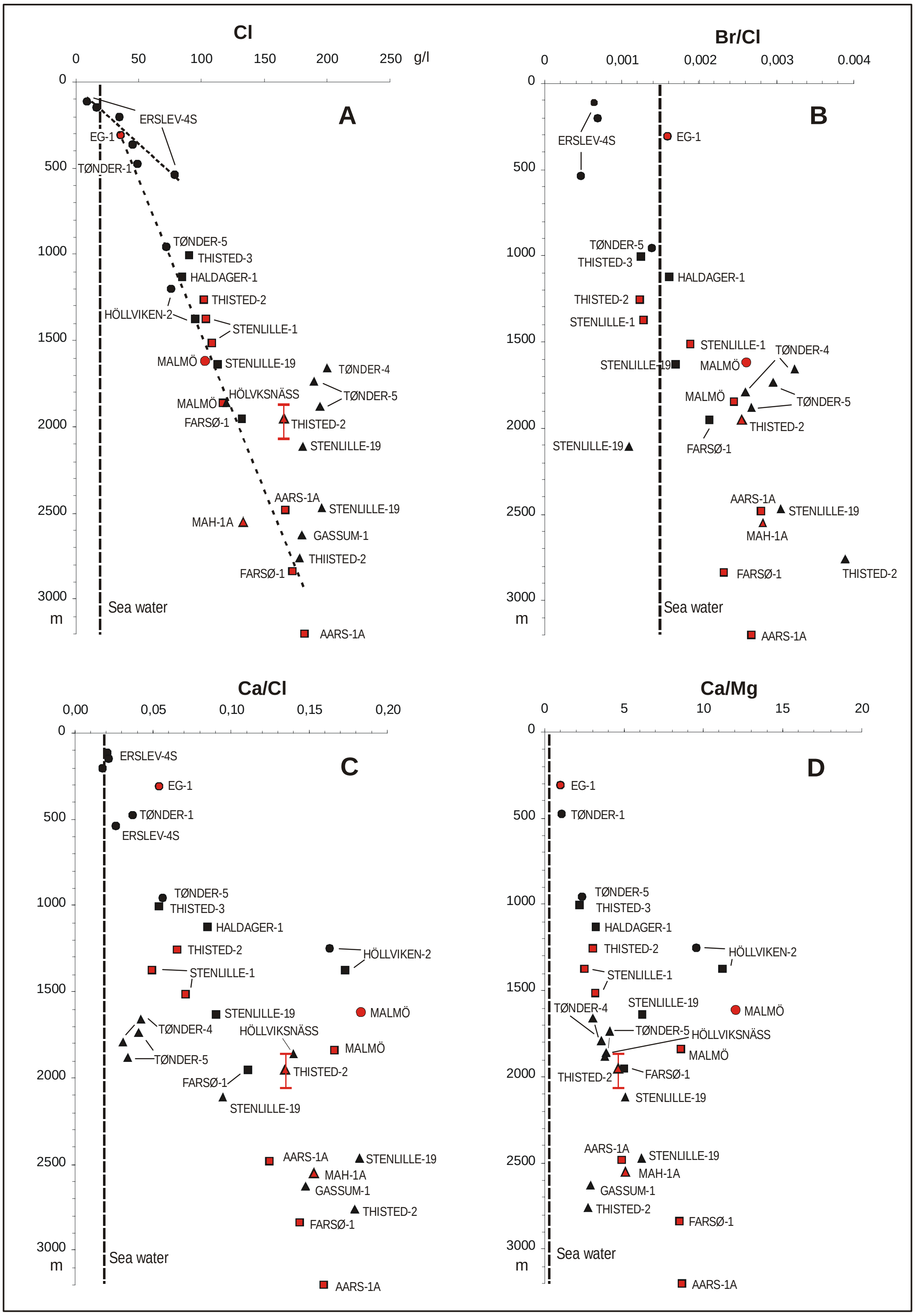

Fig. 2. *Chemistry of formation waters in the Danish sub basin. Triangles = Triassic, squares = Jurassic and circles = Cretaceous-Tertiary. Ion-ratios are in mole units. Red indicate most reliable data, usually from well tests lasting more than one day*

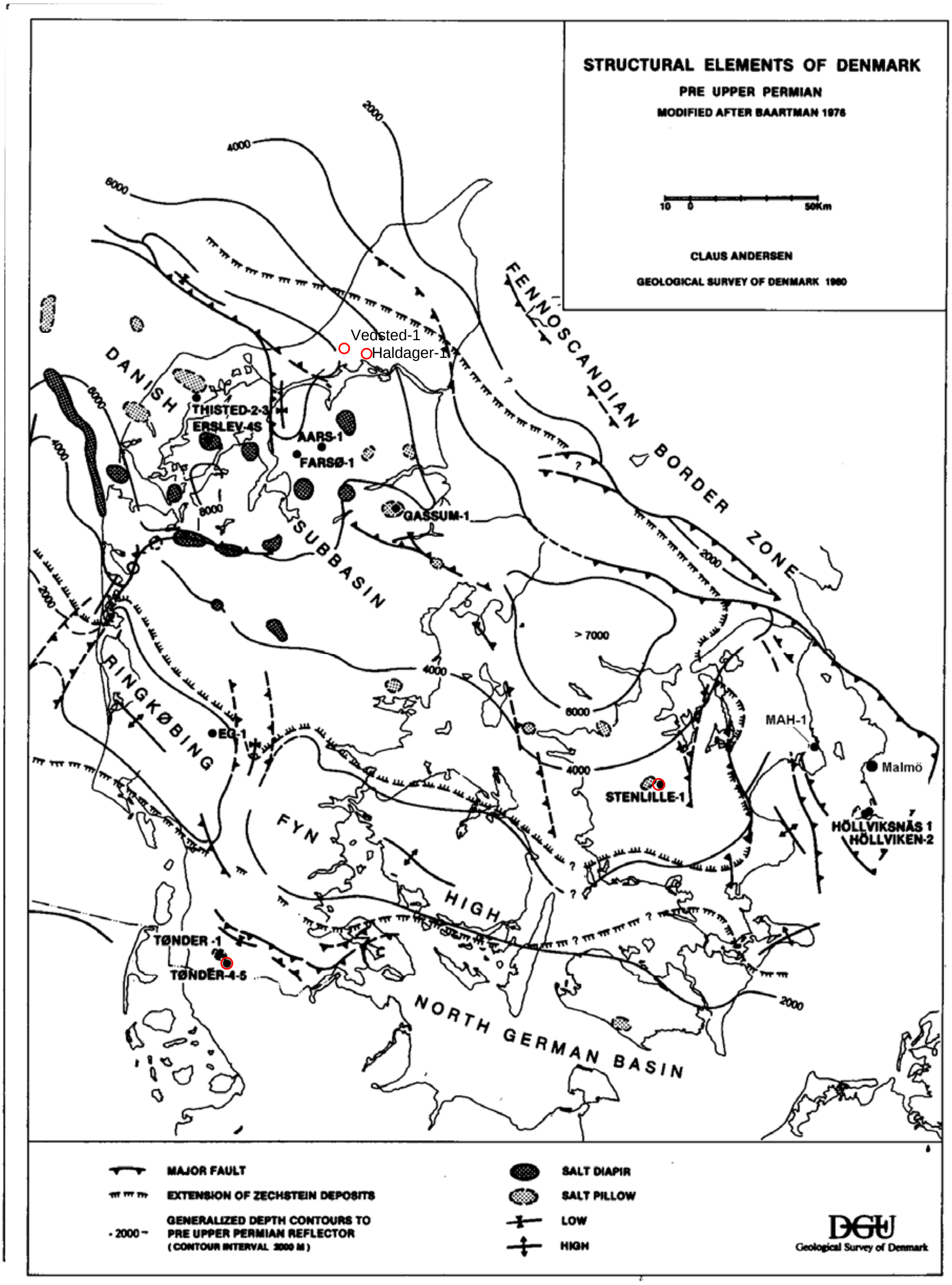

Fig. 3. *Location map indicating the position of wells from which data on formation water chemistry have been obtained. Red circles indicate position of wells from which cores samples have been selected.*

Sulphate, one of the major ions of seawater (2800 mg/L), is often quite low in formation waters due to the microbial process of sulphate reduction. Sulphate concentration is often below 50 mg/L in waters of geological formations containing organic matter. In organic lean formations like chalk and the reddish brown terrigeneous Triassic deposits sulphate concentration may be higher.

Formation waters in the area outside the massive Zechstein deposits indicated on Figure 3 do not differ significantly from waters within the area with respect to chemical composition, as is seen for data obtained from wells in southernmost Sweden (Figs. 2 and 3). The high salinity of the formation waters outside the Zechstein area may also be related to salt deposits, although very little is known about the migration mechanism in the area. Alternatively, the increase in salinity with depth outside Zechstein salt deposits area may primarily be due to hyper-filtration.

Fluid chemistry recommended for laboratory tests

Approximate formation water chemistry for the formations represented by the cores listed in Table 1 has been shown in Table 6.

Table 6. *Assumed fluid chemistry of original pore water in selected core samples*

Test No.	1	2		3	4	5	6	7
Formation	Gassum	Gassum		Haldager	Børglum	Fjerritslev	BunterSSt	Skagerrak
Well	Stenlille-18	Vedsted-1		Vedsted-1	Haldager-1	Stenlille-1	Tønder-4	Vedsted-1
Depth, m	1662	2009		1150	1041	1500	1662	2064
pH	6.2	6.6	-	6.4		6.4		6.6
Cl	113	166	*132*	102	90	103	200	166
SO4	0.015	0.29	*0.05*	0.01	0.05	0.015	0.5	0.29
Br	0.44	0.98	-	0.29	0.3	0.31	1.5	0.98
HCO3	0.08	0.03	-	0.043		0.061		0.03
Na	59	70	*63*	55	46	58	115	70
Ca	11.5	23.5	*16*	7.5	8.11	5.7	9.5	23.5
Mg	1.6	3.34	*2.1*	1.50	1.55	1.40	1.9	3.34
K	1.1	1.88	*0.35*	0.25	0.24	0.29	1.7	1.88
Sr	0.66	0.62	*0.6*	0.38	0.5	0.6		0.62
Fe	0.06	0.03	-	0.04		0.03		0.03
	Stenille-19	*Thisted-2*	*Farsø-1*	*Thisted-2*	*Haldager-1*	*Stenille-1*	*Tønder-4*	*Thisted-2*
	Gassum	*Skagerrak*	*Haldag.*	*Gassum*	*DST#3*	*Fjerritslev*	*BunterSSt*	*Skagerrak*

Concentrations are given in mg/L. Chemistry data were based on well information shown in italics. The two possibilities for Gassum of Vedsted-1 are discussed in the text.

Data on formation water chemistry concerning the Fjerritslev Formation of the Stenlille-1 well and Bunter Sandstone Formation of the Tønder-4 well were obtained from waters collected close to the actual position of the core samples selected for laboratory test. Therefore, the formation water chemistry data are considered highly reliable in this case. For the Børglum Formation of Haldager-1 well the formation water chemistry is probably not very different from that of the sandstone 100 metres below, which was tested by DST#3. However, the sodium chloride concentration shown in Table 4 was adjusted to fit chloride concentration of the deepest sample recovered from the drill string (Dinesen, 1961), placing the Haldager-1 well close to stippled line of Fig. 2a.

The rest of the data were taken from nearest wells, which of course make the data less certain. However, the uncertainty is probably minor for the Gassum Formation of the Stenlille-18 well as the distance to the Stenlille-19 well for which chemistry data exist is only 500 m. Formation water from Stenlille-19 was obtained from an air-lift test, which make data on pH, HCO_3 and Fe uncertain. Therefore, data for the three parameters were taken from the Gassum Formation of the Stenlille-1 well, located 1700 m from Stenlille-18. For the Haldager Formation of the Vedsted-1 well we find that the Gassum Formation water chemistry of the Thisted-2 well is an appropriate choice, although the distance between the two wells is approximately 55 km.

For the lab experiments to be performed on samples from the Gassum and the Skagerrak formations of the Vedsted-1 well (2009-2064 m) one could choose formation water chemistry data from either the Farsø-1 or the Thisted-2 wells, see Fig. 2a. From the well logs it appears that the depth interval (2009-2064 m) represents mostly terrigeneous deposits of late Triassic as is the case for the Skagerrak formation of Thisted-2, whereas the Haldager Sand Formation of the Farsø-1 well represents Middle Jurassic marine deposits. The salinity relative to depth appears to be to higher for Triassic formation waters compared to Jurassic formation waters (Thisted-2 and Stenlille-19 in Fig. 2a). This may be due to a more arid climate during the Triassic, which may have lead to an increase in salinity locally. Triassic evaporates were encountered in the Oddesund-1 well approximately 60 km south of the Thisted-2 well. From these considerations we conclude that the Thisted-2 Skagerrak Formation water chemistry will be the appropriate for lab experiments on the Vested-1 well core samples from 2009-2064 m

In the above attempts has been made to approximate pore fluid chemistry as precisely as possible for the formations represented by the core samples selected for lab experiments. However, given the reasonably narrow variation in formation water chemistry with depth and well location presented above, the uncertainty is not considered to be of great importance for the laboratory tests to be performed.

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