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## **ECO<sub>2</sub>: Sub-Seabed CO<sub>2</sub> Storage: Impact on Marine Ecosystems**

### **D2.1: Geochemical report on formation fluids from CO<sub>2</sub> storage sites**

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## Executive Summary

A sample of formation water from the Utsira Formation has been obtained from close to the site of CO<sub>2</sub> injection into this sub-seafloor CO<sub>2</sub> storage reservoir in the northern North Sea. The temperature of the fluid is 27.8 °C, consistent with the geothermal gradient in this area.

Here, we report the chemical composition of the formation water sample, with the aim of identifying tracers of seepage of formation water from the sub-seafloor storage reservoir.

The Na and Cl content (salinity) of the formation fluid is close to that of seawater, as are levels of Rb, Sr, Br and Sb. Concentrations of Mg, K and Ca are between 20 and 50% lower than seawater. The fluids are significantly depleted in SO<sub>4</sub>, which suggests that levels of dissolved oxygen are very low in the reservoir fluids. Li, B and Si are all enriched in the formation fluids, due to reaction with the reservoir sands. Addition of Sr from the sands is indicated by the <sup>87</sup>Sr/<sup>86</sup>Sr ratio of the formation fluids, which is higher than modern-day seawater. Concentrations of the trace metals are also higher than seawater, but this may be the result of contamination during the sampling procedure.

We conclude that Li is likely to be the best tracer of seepage of formation fluids. The Li concentration of the formation fluid is some 15 times higher than bottom seawater, and Li is relatively unreactive with the overlying sediments.

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## 1. Introduction

The Sleipner sub-seafloor carbon dioxide (CO<sub>2</sub>) storage site in the North Sea has been operated by Statoil since 1996. Since that time, more than 14 million m<sup>3</sup> of CO<sub>2</sub> recovered during extraction of natural gas has been injected into sands of the 'Utsira Formation', a storage reservoir located at depths of between 550 to 1500 m beneath the seafloor in the central parts of the northern North Sea. The Utsira formation extends for more than 400 km from north to south, and between 50 to 100 km from east to west, and is Miocene-Pliocene in age (Eidvin et al., 1999). The sands are overlain by thick Pliocene shales (the Nordland shales; Gregersen et al., 1997), which are thought to provide an effective seal for the storage reservoir. The Utsira Formation is highly porous (35 – 40%) and extremely permeable (Zweigel et al., 2004), with a total volume of pore space of  $6 \times 10^{11}$  m<sup>3</sup> (Arts et al., 2004). Prior to CO<sub>2</sub> injection, this pore space was filled entirely with so-called 'formation fluids'. On injection of CO<sub>2</sub>, the formation fluids are displaced by the gas, and some of the CO<sub>2</sub> will dissolve into them.

To date, there is sparse information on the chemical composition of these formation waters. It is essential to fill this gap, because displacement and subsequent seepage of formation water could occur during CO<sub>2</sub> injection, and may therefore act as a precursor to CO<sub>2</sub> seepage. Moreover, Statoil have already observed a number of seeps in the vicinity of the injection site where shallow gas is being emitted into the water column. Some of these seeps are associated with abandoned exploration wells.

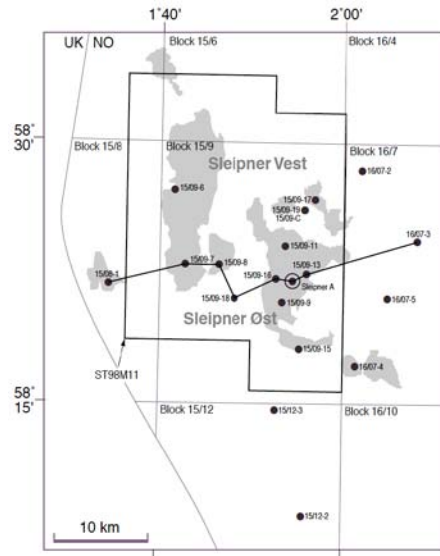
Thus, one of the objectives of the ECO2 project is to characterise the chemical composition of formation fluids from existing sub-seafloor CO<sub>2</sub> storage reservoirs. These included Sleipner and Snøhvit. However, as water is not produced at Snøhvit, it has not been possible to obtain a sample of the formation fluids to date. If a new well is drilled at this location, within the timeframe of ECO2, then Statoil will endeavour to provide us with a sample. Nevertheless, Utsira formation fluids are currently being produced at one development wellbore. Statoil have provided us with a sample of this fluid, and here we report the results of analysis of its chemical composition. This includes concentrations of the anions, and major, minor and trace cations (including metals), as well as strontium isotopes.

## 2. Sample Collection

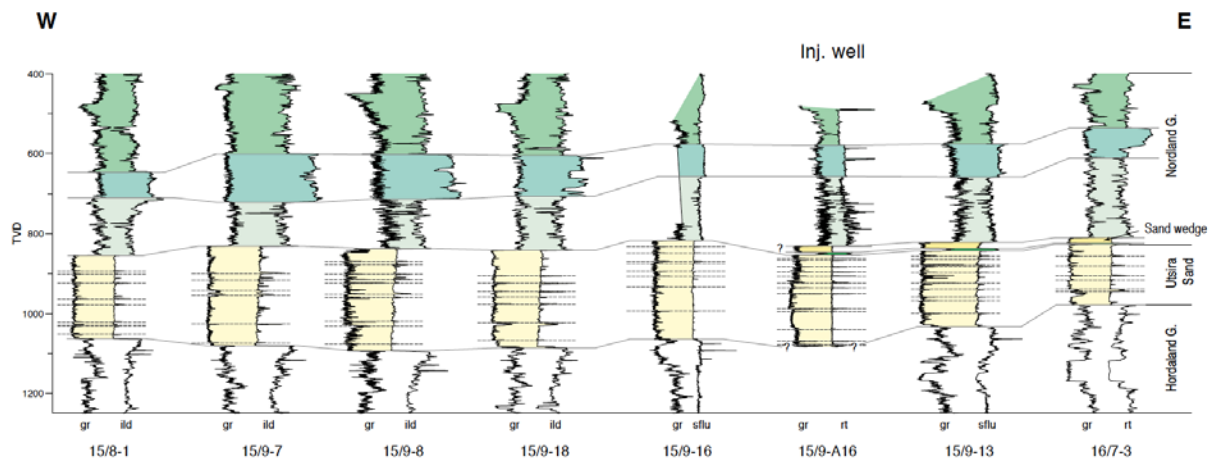
A sample of Utsira formation fluid was collected on 19 February 2011 from wellbore 15/9-F-07, located at 58° 26' 29.87" N, 1° 53' 14.86" E at a water depth of 91 m (Fig 1). The wellbore penetrates the Utsira sands between ~850 – 1050 m below seafloor (Fig. 2).

The fluid was recovered from the well by Statoil engineers and immediately sampled into a HDPE bottle. The sample was not treated in any way, which precluded analysis of any time sensitive species (pH, alkalinity, dissolved inorganic carbon, stable carbon and oxygen isotopes) or gases (methane, CO<sub>2</sub>, noble gases) that would have been of interest. It is important to note that the sample was not collected using usual 'clean' sampling procedures, potentially compromising the analysis of metals and other trace species.

On arrival in Southampton, the sample was filtered through a 0.4  $\mu\text{m}$  cellulose acetate membrane filter, and split into two aliquots. One aliquot was acidified with thermally-distilled (TD)  $\text{HNO}_3$  to 1%; both aliquots were subsequently stored in the fridge at 4  $^\circ\text{C}$ .



**Fig. 1:** Position of wellbore 15/9-F-07 in the Norwegian block of the Northern North Sea. The line running from east to west depicts the well section shown in Fig. 2.  $\text{CO}_2$  injection occurs at wellbore 15/9-16A, which is labelled Sleipner A. After Zweigel et al. (2004).



**Fig. 2:** West-East oriented well profile through the Utsira sand and its cap rock in the Sleipner area. Wellbore 15/9-F-07 is shown second left. The log peaks within the Utsira sand are interpreted to indicate the presence of thin shale layers.  $\text{CO}_2$  injection occurs at wellbore 15/9-16A. After Zweigel et al. (2004).

### 3. Analytical Methodology

#### 3.1 Cations

Cation concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin-Elmer Optima 4300 DV) or inductively coupled plasma mass spectrometry (ICP-MS; Thermo Scientific X-Series 2) at the National Oceanography Centre, Southampton. Lithium (Li), boron (B), sodium (Na), magnesium (Mg), silica (Si), potassium (K), calcium (Ca), strontium (Sr) and barium (Ba) concentrations were all determined by ICP-OES, and Mg, K, Ca, vanadium (V), manganese (Mn), iron (Fe), nickel (Ni), zinc (Zn), rubidium (Rb), molybdenum (Mo), antimony (Sb) and thorium (Th) concentrations were determined by ICP-MS. Note that levels of Mg, K and Ca were determined using both methods.

Parameter	Setting
Autosampler	Perkin-Elmer AS93 Plus
Nebulizer	Glass expansion concentric
Spray chamber	Glass expansion cyclonic
Carrier gas flow rate	0.70 L/min
Plasma view orientation	Dual view: axial & radial
Detector integration time	100 – 200 ms
Detector read time	10 s

**Table 1:** Instrument parameters for ICP-OES analyses

For ICP-OES analyses, the sample was diluted by a factor of 40 with 2% TD HNO<sub>3</sub>, and cation concentrations were determined using the settings given in Table X. Standards were prepared from single element standard solutions that covered the expected range of concentrations. A seawater certified standard reference material (CRM-SW; High Purity Standards) was analysed as an ‘unknown’ alongside the sample. Results of replicate analysis of this material are given in Table 2. The reproducibility of the analyses, based on four replicate analyses of the Utsira formation fluid sample, was better than ±1% for all elements (1σ, where σ is the standard deviation).

CRM-SW	Li ng/g	B µg/g	Na mg/g	Mg mg/g	Si µg/g	K µg/g	Ca µg/g	Sr µg/g	Ba ng/g
Av. measured (±1σ std dev; n=5)	95.0±1.7	5.06±0.05	10.5±0.14	1.25±0.006	4.26±0.02	378±4.4	405±0.8	12.0±0.29	51.2±3.4
Certified range	95-105	4.9-5.1	10.5-10.6	1.24-1.26	3.9-4.1	378-382	398-402	11.9-12.1	49-51

**Table 2:** Results of replicate analysis of the certified seawater reference material CRM-SW by ICP-OES, together with the certified values.

For ICP-MS analyses, samples were diluted by a factor of 500 with 2% TD HNO<sub>3</sub>. A mixed spike solution, consisting of In, Re and Be, was added to both the samples and standards in order to monitor instrument drift. Standards were prepared by mixing single element standard solutions, and a variety of standard references materials (including rocks, river water and seawater) were run at the same time to assess the accuracy of the analyses. This was better than ±5% for all elements. Analytical reproducibility, determined by repeat analysis (n = 3) of the Utsira formation water

samples, is better than  $\pm 2\%$  for Mg, K, Ca, Mn, Zn, Rb and Th, and better than  $\pm 5\%$  for V, Fe, Ni, Mo and Sb.

### **3.2 Anions**

Concentrations of chloride (Cl), bromide (Br) and sulphate ( $\text{SO}_4$ ) were determined by ion chromatography (IC; Dionex ICS2500). The unacidified sample aliquot was diluted by a factor of 100 with Milli-Q water, and transferred to autosampler tubes. Standards were prepared from single anion solutions, and accuracy was assessed by analysis of a seawater reference material. Measured anion concentrations for the reference material were always in the range of the certified values. The reproducibility of the analyses, determined by repeat analysis of the reference material, was better than 0.1% for Cl and better than 2% for Br and  $\text{SO}_4$ .

### **3.3 Strontium isotope ratios**

Strontium was separated from the rest of the sample matrix using Sr-spec resin. Briefly,  $\sim 100 \mu\text{l}$  of Utsira formation water was dried down and re-dissolved in  $200 \mu\text{l}$  of 3M TD  $\text{HNO}_3$ . This was loaded onto a column containing pre-cleaned Sr-spec resin. The matrix was eluted with 2.5 ml of 3M TD  $\text{HNO}_3$ , and the Sr was collected with 1.5 ml of Milli-Q water. The Sr fraction was then dried down ready for loading for analysis by thermal ionisation mass spectrometry (TIMS).

$1 \mu\text{l}$  of tantalum (Ta) activator was added to a Ta filament and dried down slowly at 0.8 A. The Sr fraction was re-dissolved in  $1.5 \mu\text{l}$  of 1M TD HCl, and loaded on to the filament  $\sim 0.5 \mu\text{l}$  at a time. The current was slowly turned up to 2A until the filament glowed.

The loaded sample was transferred to the TIMS (Thermo Scientific TritonPlus) to determine the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic composition. 150  $^{87}\text{Sr}/^{86}\text{Sr}$  measurements were made per sample, and the ratios were internally normalised to  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ . Analytical reproducibility was assessed by replicate analysis of the NBS 987 Sr isotope standard. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of this standard was  $0.710244 \pm 0.000019$  ( $2\sigma$ ,  $n = 135$ ).

## **4. Results**

The chemical composition of the Utsira formation fluid sample is reported in Table 3. Results of analysis of North Atlantic seawater are also shown for comparison.

### **4.1 Temperature**

The temperature of Utsira formation water, measured on retrieval of the sample at the head of the wellbore, was  $27.8 \text{ }^\circ\text{C}$ .

### **4.2 Anions**

The Cl content of the Utsira formation water ( $529 \text{ mmol/L}$ ) is similar to seawater ( $540 \text{ mmol/L}$ ). The Br concentration ( $1310 \mu\text{mol/L}$ ) is slightly higher than seawater ( $830 \mu\text{mol/L}$ ), whereas the concentration of sulphate is very low ( $10 \mu\text{mol/L}$ , compared to  $28 \text{ mmol/L}$  in seawater).

### 4.3 Alkali and alkaline earth elements

Like Cl, the concentration of Na in Utsira formation waters (470 mmol/kg) is close to seawater (460 mmol/kg), as is the concentration of Rb (1.06  $\mu\text{mol/kg}$ , compared to 1.3  $\mu\text{mol/kg}$  in seawater). Concentrations of K and Mg (respectively, 5.9 mmol/kg and 23.3 mmol/kg) are approximately half those of seawater (K = 10 mmol/kg, Mg = 52 mmol/kg), whereas the Sr content of Utsira formation waters (93.3  $\mu\text{mol/kg}$ ) is slightly higher than seawater (88  $\mu\text{mol/kg}$ ). The Ba and Li content of the reservoir formation fluid (respectively, 4.16  $\mu\text{mol/kg}$  and 398  $\mu\text{mol/kg}$ ) is an order of magnitude higher than seawater (Ba = 0.15  $\mu\text{mol/kg}$ , Li = 25  $\mu\text{mol/kg}$ ).

Species	Units	Technique	Utsira formation water	North Atlantic seawater
<i>Cations</i>				
Li	$\mu\text{mol/kg}$	ICP-OES	398	25
B	$\mu\text{mol/kg}$	ICP-OES	1450	410
Na	mmol/kg	ICP-OES	470	460
Mg	mmol/kg	ICP-OES	22.5	52
Mg	mmol/kg	ICP-MS	24.1	52
Si	$\mu\text{mol/kg}$	ICP-OES	979	~0.13
K	mmol/kg	ICP-OES	5.79	10
K	mmol/kg	ICP-OES	5.95	10
Ca	mmol/kg	ICP-OES	7.90	10.1
Ca	mmol/kg	ICP-MS	8.03	10.1
V	$\mu\text{mol/kg}$	ICP-MS	2.57	0.03
Mn	nmol/kg	ICP-MS	44.3	~1
Fe	nmol/kg	ICP-MS	390	~0.1
Ni	nmol/kg	ICP-MS	59.6	~3
Zn	nmol/kg	ICP-MS	2700	~0.5
Rb	$\mu\text{mol/kg}$	ICP-MS	1.06	1.3
Sr	$\mu\text{mol/kg}$	ICP-OES	93.3	88
Mo	nmol/kg	ICP-MS	11.9	1
Sb	nmol/kg	ICP-MS	2.03	1.7
Ba	$\mu\text{mol/kg}$	ICP-OES	4.16	0.15
Th	nmol/kg	ICP-MS	33.4	0.04
<i>Anions</i>				
Cl	mmol/L	IC	529	540
Br	$\mu\text{mol/L}$	IC	1310	830
SO <sub>4</sub>	$\mu\text{mol/L}$	IC	10	28000
<i>Isotopes</i>				
<sup>87</sup> Sr/ <sup>86</sup> Sr		TIMS	0.709237	0.70918

**Table 3:** Chemical composition of Utsira formation water sampled from wellbore 15/9-F-07. The composition of North Atlantic seawater is also shown for comparison.

### 4.4 Trace metals

Concentrations of V, Mn, Fe, Ni, Zn and Mo are all significantly higher than in seawater. This may be real, but it may also be the result of contamination during the sampling procedure (see Section 2).

### 4.5 B, Si, Sb and Th

Concentrations of Si and Th in Utsira formation water (respectively, 979  $\mu\text{mol/kg}$  and 33.4 nmol/kg) are approximately 3 orders of magnitude higher than seawater (Si  $\approx$  0.13  $\mu\text{mol/kg}$ , Th = 0.04 nmol/kg). Levels of B (1450  $\mu\text{mol/kg}$ ) are also higher than seawater (410  $\mu\text{mol/kg}$ ), but only by a factor of  $\sim$ 4. By contrast, the concentration of Sb (2.03 nmol/kg) is similar to seawater (1.7 nmol/kg).



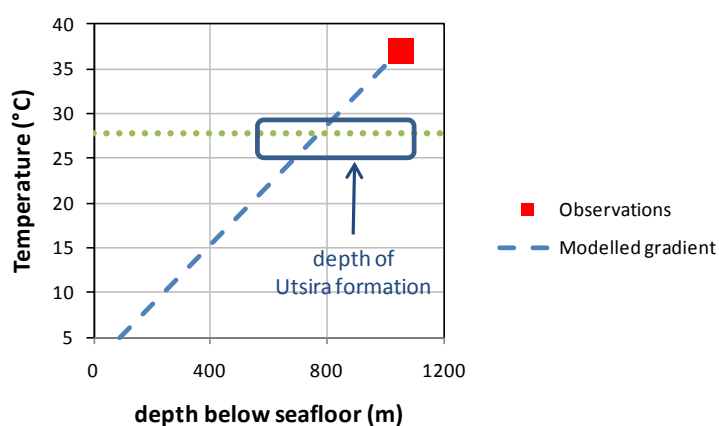
## 4.6 $^{87}\text{Sr}/^{86}\text{Sr}$

The Sr isotopic composition ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) of Utsira formation water is 0.709237, which is slightly higher (slightly more radiogenic) than modern-day seawater (0.70918).

## 5. Discussion

### 5.1 Temperature

The temperature of the formation fluid (27.8 °C) is consistent with a single previous measurement (37 °C at a depth of 1058 m below seafloor: Lindeberg et al., 2000; Zweigel et al., 2004), and with the modelled geothermal gradient, at the depth of the Utsira formation in the Sleipner area (Fig. 3; Lindeberg et al., 2000).



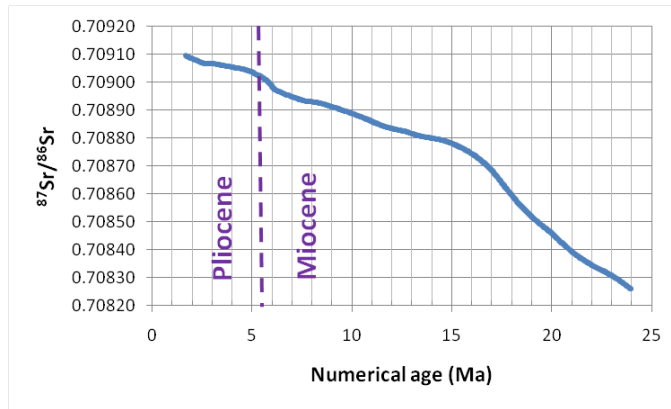
**Fig. 3:** Observations (red square) and modelled geothermal temperature gradient in the Sleipner area (Lindeberg et al., 2000). Green dotted line shows the temperature of our formation water sample; blue box shows the depth range of the Utsira formation.

### 5.2 Origin of Utsira formation waters

In contrast to many formation waters, Utsira waters are not particularly saline, and their Na-Cl content is close to that of seawater. Concentrations of  $\text{SO}_4$  are very low, which may imply reducing conditions and bacterial sulphate reduction. This is consistent with relatively high levels of dissolved Fe, although it is important to note that contamination of the sample during the extraction procedure may also have increased levels of Fe. An alternative possibility is that concentrations of  $\text{SO}_4$  have never been high in Utsira formation waters, for example if they are sourced from glacial waters or evaporites, but their seawater-like Na-Cl content would appear to exclude this.

The silica content of the formation waters is much higher than seawater, presumably because of reactions between the formation waters and the reservoir sands. Indeed, the concentration of Si measured in our sample (979  $\mu\text{mol}/\text{kg}$ ) is entirely consistent with control by silica solubility, calculated at the fluid temperature ( $\sim 28$  °C) and reservoir depth ( $\sim 80$  bar), which is  $\sim 1$  mmol/L (Fournier and Marshall, 1983).

The Sr isotopic composition of the formation water also indicates that the fluids have interacted with the reservoir sands. Given that the reservoir is Miocene-Pliocene in age (Eidvin et al., 1999), the expected  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the unreacted formation fluid is in the range 0.708260 to 0.709085 (Fig. 4; McArthur et al., 2001). The measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of Utsira formation water is 0.709085, which is higher even than modern-day seawater (0.70918), consistent with addition of radiogenic Sr from silicate minerals (such as feldspar grains) in the Utsira sands.



**Fig. 4:** Seawater Sr isotope curve for the Miocene (23.8 to 5.32 Ma) and Pliocene (5.32 to 1.77 Ma), the reported age range of the Utsira formation. After McArthur et al. (2001).

High levels of Li and B may also be due to reaction of the formation fluids with the reservoir sands. Dissolution of B and Li from silicate minerals occurs at moderate temperatures (e.g. James et al., 2003; Wimpenny et al., 2010). Rb is not usually leached at moderate temperature (James et al., 2003), which is also consistent with our observations.

Although Th is added to the fluid phase during water-rock reactions, its concentration is generally low because Th is rapidly scavenged from solution (Andersson et al., 1995; Chabaux et al., 2003). The high concentrations measured in Utsira formation fluids is therefore unexpected, and may reflect contamination during the sampling procedure.

### **5.3 Comparison with previous data**

To our knowledge, there is only one existing report of the chemical composition of Utsira formation waters, which is restricted to Na, Ca, Mg, Fe, Sr, K, Cl,  $\text{SO}_4$  and Sr, oxygen and hydrogen isotopes (Munz et al., 2010; Table 4). The fluids were collected from wellbores E-10 (60° 42' 1.79" N, 2° 56' 6.76" E) and E-13 (60° 42' 1.72" N, 2° 56' 6.76" E), in the 30/6 sector of the Norwegian North Sea. These wellbores lie ~260 km north of wellbore 15/9-F-07, and they penetrate the Utsira formation at a depth of 720 – 890 m below seafloor. Water is actively extracted and injected into exploration wells in this sector for pressure support.

The Na and Cl contents of the different samples are very similar, as are concentrations of Mg and K. Concentrations of Ca, Ba and Sr are slightly higher in the waters produced in sector 30/6, as are concentrations of  $\text{SO}_4$ . This may be indicative of precipitation of  $\text{CaSO}_4$  and  $\text{BaSO}_4$  minerals in sector 15/9, either within the formation itself or during sample recovery. Precipitation of carbonate phases, however, is another possibility.

Species	Units	Wellbore/ sampling date				
		15/9-F-07† 19/02/11	E-10* 03/11/00	E-10* 09/11/00	E-10* 12/03/03	E-13* 12/03/03
<i>Cations</i>						
Na	mmol/kg	470	455	450	443	450
Mg	mmol/kg	23.3	26.2	23.9	23.6	21.9
K	mmol/kg	5.87	8.0	6.6	6.6	8.3
Ca	mmol/kg	7.97	16.4	16.2	16.2	15.3
Fe	nmol/kg	390	1790	1790	107000	<89500
Sr	μmol/kg	93.3	144	132	137	126
Ba	μmol/kg	4.16	45.9	31.3	36.4	36.4
<i>Anions</i>						
Cl	mmol/L	529	522	509	516	528
SO <sub>4</sub>	μmol/L	10	948	219	31	<208
<i>Isotopes</i>						
<sup>87</sup> Sr/ <sup>86</sup> Sr		0.709237	n/a	n/a	n/a	0.708768
δ <sup>18</sup> O	‰ VSMOW	n/a	n/a	n/a	n/a	-0.9
δD	‰ VSMOW	n/a	n/a	n/a	n/a	-8.1

**Table 4:** Comparison of chemical composition of Utsira formations waters produced in sectors 15/9 (wellbore 15/9-F-07) and 30/6 (wellbores E-10 and E-13) of the Norwegian North Sea. †This study. \*Data from Munz et al. (2010).

Interestingly, the <sup>87</sup>Sr/<sup>86</sup>Sr ratio of the fluids recovered from wellbore 30/6-E-13 is rather lower than the ratio we measure for fluid recovered from wellbore 15/9-F-07. The value measured in wellbore 30/6-E-13 (0.708768) is consistent with seawater of Miocene age (Fig. H), which indicates minimal addition of radiogenic Sr from the reservoir sands. The shallower depth of the reservoir means that temperature is lower, which may inhibit reaction between the formation fluids and the reservoir rocks. As no Si (or Li or B) data are available for wellbore 30/6-E-13 fluids we cannot, however, confirm this.

#### 5.4 Potential precursors of CO<sub>2</sub> leakage from storage reservoirs

In theory, chemical species that have significantly different concentrations in formation fluids compared to bottom seawater will be the best tracers of seepage from the CO<sub>2</sub> storage reservoir. However, because the chemical signature of some species will be modified as the fluid passes through the sedimentary overburden, only species that are largely unreactive will be useful to this end. Thus, although for example concentrations of Fe in the formation fluids are far higher than they are in bottom seawater (Table 3), this redox-active element will be modified by diagenetic reactions in the overlying sediments, which may remove or add Fe to the upwelling fluid.

Na and Cl are relatively unreactive, yet their concentration in Utsira formation fluids is unfortunately very close to bottom seawater. This is also true for Sr and K, and for <sup>87</sup>Sr/<sup>86</sup>Sr. The best tracer of seepage of Utsira formation fluids is likely to be Li. Li concentrations in the formation fluids are some 15 times higher than they are in bottom seawater, and Li is relatively unreactive at low temperature (e.g. You et al., 1995).

## 6. Conclusions

Analysis of the chemical composition of Utsira formation fluids from wellbore 15/9-F-07 reveals that their Cl and Na content is similar to that of bottom seawater. Formation fluids recovered from the

Utsira formation from other wellbores, some 260 km to the north, contain similar levels of Na and Cl.

The fluids from wellbore 15/9-F-07 have very low concentrations of  $\text{SO}_4$  (3 orders of magnitude lower than seawater) which implies that levels of dissolved oxygen in the reservoir are low. Elevated levels of Si, Li and B relative to seawater imply reaction between the formation fluids and the reservoir sands; the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the formation fluids is higher than that of Miocene-Pliocene-aged seawater, which is consistent with input of radiogenic Sr from the reservoir sands.

Concentrations of trace metals in the formation fluids are significantly higher than they are in bottom seawater. However, we cannot rule out contamination of the sample during collection, so the data that we present here should be viewed with caution.

We conclude that the best tracer of seepage of formation fluids from the Sleipner sub-seafloor  $\text{CO}_2$  storage reservoir is Li. This element is significantly enriched ( $\times 15$ ) in the formation fluids relative to seawater, and is relatively unreactive during transport through the overlying sediment column.

### ***Acknowledgements***

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