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# **Applicability of Noble Gases for CO<sub>2</sub> Capture and Storage Monitoring**

**Thesis submitted for the degree of Philosophiae Doctor**

Department of Geosciences

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# Preface

This dissertation has been submitted to the Department of Geosciences at the Faculty of Mathematics and Natural Sciences in accordance with the requirements for the degree of Philosophiae Doctor (Ph. D.). The research presented here was conducted at the University of Oslo and at Eawag/ETH Zürich, under the supervision of Dr. Anja Sundal, University of Oslo, Prof. Rolf Kipfer, ETH Zürich and Eawag, Switzerland, Prof. Philip Ringrose, NTNU Trondheim, Norway, and Dr. Matthias Brennwald, Eawag, Switzerland. This work was a part of the ICO<sub>2</sub>P project which was supported by the Norwegian Research Council through a CLIMIT grant (project number 280551) with financial contributions from Equinor and Shell.

The thesis is a collection of three published papers, and one manuscript, presented in chronological order of writing. The papers are preceded by a synopsis that motivates the research objectives and the approach to address those objectives. The synopsis includes a summary of the papers, relates them to each other and gives an outlook on future research.

## Acknowledgements

This thesis was written in turbulent times. The COVID-19 pandemic is still going on and weather extremes, a consequence of man-made global warming, have become more and more frequent. Both have caused huge damages. Luckily, Norway has been relatively spared of both and I have had a safety net of supervisors, colleagues, friends and family, that allowed for an enjoyable and hopefully successful time. If, in the end, I have been a small cog in the wheel of climate change mitigation science, I would be more than happy.

My main supervisor Anja Sundal (University of Oslo) led this safety net with her sheer endless positivity and optimism, and more than once pushed some of my scepticism away. She made me try and experiment without boundaries which paved the way for unforgettable experiences. Rolf Kipfer (Eawag/ETH Zurich), as co-supervisor, had always sound advice ready, not only in science but also in life. Without him, I would not have gone to Norway in the first place. I would not have been on a research cruise when the pandemic broke out staying mostly unaffected of the worst lockdown. Without co-supervisor Philip Ringrose's (NTNU Trondheim/Equinor) knowledge of the CCS world and the connection to the industry, facilitating some of the essential samples, this work would not have been possible. I thank co-supervisor Matthias Brennwald (Eawag) for his help with the nitty-gritty of the sampling and analyses. Even though not an official supervisor, the cooperation with Niko Kampman (Shell) was so essential, that I am inclined to include him in this paragraph. Thank you all for your trust and guidance.

Furthermore, I would like to thank the administration at the department and the faculty at the University of Oslo and the Research Council of Norway for providing the organisational and financial framework to conduct this work. This has been the backbone of my scientific freedom. The possibility to participate in conferences, summer schools and conduct fieldwork shall not be taken for granted.

I am grateful for the smooth work during the different field and lab campaigns, which was made possible by great people: Anette Beate Nesse Knarvik, Nina Enaasen Flø and Magnus Aronsson at the Technology Center Mongstad, Kim Johnsen Håkon, Knudsen Olset at Melkøya, Jørgen Thomassen at Klemetsrud, Edith Horstmann and Colin Maden at the ETH laboratory, Christian Hensen as representative for the whole 'Meteor' crew and the extraordinarily kind Yves Reeht, representative for the whole 'Johan Hjort' crew. Unfortunately, I could not do more fieldwork at Mont Terri, but working with Antonio Pio Rinaldi and Clement Roques, even though mostly remotely, was a pleasure. Also not in person, but through many conversations, Anne-Karri Furre (Equinor) was very helpful and inspiring to work with.

I am grateful for my colleagues here at the University of Oslo making work to such a pleasant environment in countless coffee and beer breaks. John, Mohammed, Anna, Andrea, Val, Miquel, Johnny, Sian, Thea, Camilla and many others. John(athon) Osmond deserves a special mention, since he is so helpful and his excitement for science is inspiring. During the too few times at Eawag,

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Edith, Alex and Yama were just as good colleagues. At least virtually, we could see each other frequently. All these people are colleagues but just as well friends. Special thanks to my 'colleagues', my most reliable proofreaders, aunt Ulrike and uncle Otto.

I am grateful for my Norwegian friends that made life enjoyable: my partner Solvei, Basti, Adam, Anne-Bodil and Lars. They were my substitute family not only under travel restrictions. Too many to mention namely, but thanks to the people from OSI klatring for the distractions day in and day out. I see my German friends too seldom, but just thanks for being there, Marcel, Basti and the whole crew from Worms. I miss you!

Finally, of course, my family. It has not always been easy under travel restrictions, but I know I can always count on your support and love. My parents Ilse and Helmut, my sister Ruth and my brother Paul. This work is for you.

• **Ulrich Wolfgang Weber**

Oslo, September 2021



# Abstract

Capture and subsequent geological storage of CO<sub>2</sub>, known as carbon capture and storage (CCS), is a climate change mitigation technology that is needed in most IPCC emission scenarios to restrain global warming to 1.5 °C. Measurement, monitoring and verification (MMV) strategies are set into place at storage sites to ensure safe operations, to be informed on the behaviour of the stored CO<sub>2</sub> and, ultimately, to verify that the CO<sub>2</sub> is contained long-term in the geological storage complex.

One group of tracers that has been applied successfully in MMV strategies are noble gases, which are trace constituents of all environmental fluids and are also found in the injected CO<sub>2</sub>. Divided in four central chapters, this thesis aims to advance the application of noble gases with introducing the use of portable mass spectrometers (MS) for on-site noble gas analysis into CCS research.

The first chapter demonstrates the capabilities of such a MS by developing and applying a novel approach to quantify air-water gas exchange of water bodies only by utilizing the temperature-induced changes of the solubility of noble gases in water. The method is currently most efficiently applied at water bodies with high diurnal temperature changes and it does not require artificial addition of a gas tracer.

The second chapter describes sampling campaigns performed at several CO<sub>2</sub> capture plants to characterize noble gas concentrations in the captured CO<sub>2</sub>. The noble gas content is lowered by several orders of magnitude during the capture process. It was found to be strongly dependent on the flue gas from which the CO<sub>2</sub> is captured on the one hand and by internal processes in the CO<sub>2</sub> capture plant on the other hand. Both factors induced temporal variation in the noble gases. In effect, a technology for characterizing the noble gas content of the CO<sub>2</sub> product at such capture plants more holistically is provided.

The primary focus of the third chapter is the description and execution of phase partitioning calculations between the injected CO<sub>2</sub> and the pore-water of a storage formation based on the previously acquired datasets. The exchange with the pore-water, i.e. the stripping of noble gases into the injected CO<sub>2</sub>, will cover the inherently low noble gas concentrations and the temporal variation of the injected CO<sub>2</sub>. The stripped noble gases are sufficient to allow recognizing the CO<sub>2</sub> at single digit percent concentrations in a fluid mixture. Differences to an atmospheric noble gas signature are especially large in helium and differences to natural gas are most significant in xenon. In summary, this makes for a suitable, inherent target for leakage attribution in MMV strategies. An artificial tracer addition could further increase detectability and would be most feasible through xenon isotopes. However, in contrast to prior studies, this work derives that the tracer addition would increase MMV costs so significantly that it is

uneconomical given current financial boundary conditions of most CCS projects.

In the fourth chapter the results of an injection experiment are presented to facilitate transfer between theoretical and observational behaviour of the injected CO<sub>2</sub>. Water enriched with CO<sub>2</sub> and krypton was injected into the Opalinus Clay of the Mont Terri Rock Laboratory, which is a suitable caprock analogue. The geochemical monitoring included dissolved (noble) gases, stable isotopes and ion composition. A feasible adaption of the portable MS to a high pressure, low flow environment was developed. CO<sub>2</sub> migration was observed directly in the increasing CO<sub>2</sub> content and unambiguously low  $\delta^{13}C$  values, with which the injection water was labelled. The CO<sub>2</sub> induced chemical reactions that led to a retardation of the CO<sub>2</sub> against krypton and an observable change in the ion composition. Helium, which is commonly enriched in old pore-water, increased at the monitoring interval. The permeability of the caprock was not significantly altered and the migration of the injection water is likely limited to a discontinuous, small-scale fracture network. The experiment demonstrates that the mixing of the in-situ pore-water with the injected water would make a leakage distinguishable from atmospheric concentrations. It also indicates that some noble gases migrate faster than CO<sub>2</sub>, which could, in effect, result in an early warning function.

In conclusion, this thesis highlights how the progress of measurement technologies expands the applicability of noble gas research and the usefulness of noble gas tracers as geochemical tracers for CCS on multiple scales. The experiences gathered can be applied in further fundamental injection experiments or sampling campaigns on the partitioning behaviour in capture plants. The analyses of the acquired samples provide a reference dataset for leakage attribution at offshore sites.



# List of Papers

## Paper I

U. W. Weber, P. G. Cook, M. S. Brennwald, R. Kipfer and T. C. Stieglitz “A Novel Approach To Quantify Air-Water Gas Exchange in Shallow Surface Waters Using High-Resolution Time Series of Dissolved Atmospheric Gases”. In: *Environmental Science & Technology*, 2019, Vol. 53, no. 3, pp. 1463–1470. DOI: 10.1021/acs.est.8b05318.

## Paper II

U. W. Weber, R. Kipfer, E. Horstmann, P. Ringrose, N. Kampman, Y. Tomonaga, M.S. Brennwald and A. Sundal “Noble Gas Tracers in Gas Streams at Norwegian CO<sub>2</sub> Capture Plants”. In: *International Journal of Greenhouse Gas Control*, 2021, Vol. 106, DOI: 10.1016/j.ijggc.2020.103238.

## Paper III

U. W. Weber, N. Kampman and A. Sundal “Techno-Economic Aspects of Noble Gases as Monitoring Tracers”. In: *energies*, 2021, Vol. 14, no. 12 DOI: 10.3390/en14123433

## Paper IV

U. W. Weber, A. P. Rinaldi, C. Roques , A. Zappone, S. Bernasconi, M. Jaggi, Q. Wenning, S. Schefer, M. Brennwald and R. Kipfer “Geochemical Evidence for Cross-Fault CO<sub>2</sub> Migration in a Caprock”. Unsubmitted manuscript, 2021



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# **Synopsis**



# Chapter 1

## Introduction

### 1.1 Motivation

The capture and subsequent geological storage of  $\text{CO}_2$ , known as carbon capture and storage (CCS), is a climate change mitigation technology that is expected to be needed to restrain global warming, as described in various IPCC reports (Metz et al. 2005; Rogelj et al. 2018; Vuuren et al. 2011). In the latest special report on pathways to limit global warming to  $1.5^\circ\text{C}$  in the 21st century, the median cumulative amount of  $\text{CO}_2$  needed to be stored through CCS until 2100 is  $865\text{ GtCO}_2$  (Rogelj et al. 2018; Zahasky et al. 2020). Even though CCS is not deployed in all of these pathways, it is useful to decarbonate the energy sector and, especially, hard-to-abate industries such as the chemical and cement industry (Ringrose 2017; Rogelj et al. 2018). As of 2020, there is a global capture capacity of  $40\text{ MtCO}_2/a$  (Global CCS Institute 2020). Comparing this figure to the necessary amounts stored it becomes evident that CCS needs to be upscaled exponentially throughout the 21st century and that with an even higher growth rate than in the past (Zahasky et al. 2020). More than ten thousand injection wells will be needed to achieve a necessary storage rate of  $6 - 7\text{ GtCO}_2/a$  by 2050 Ringrose et al. 2019. These wells and the associated storage sites need to be operated responsibly and, therefore, need some form of monitoring.

In recent years the number of operational CCS projects has increased and the number of projects in the development phase is growing strongly on a global level (Global CCS Institute 2020). Most of the operational projects target reducing emissions from natural gas processing (Global CCS Institute 2020). During the last decade, the focus of CCS has, however, shifted towards emissions from power generation and other industry emissions. Also in Norway, a full-scale CCS project called ‘Longship’ was initiated that aims to capture  $\text{CO}_2$  from a cement plant and later on from a waste incineration plant (Norwegian Ministry of Petroleum and Energy 2020). The captured  $\text{CO}_2$  will be transported by ship and stored in the Johansen and Cook formations below the seafloor of the North Sea (Norwegian Ministry of Petroleum and Energy 2020), which have been characterized as a suitable storage location (Norwegian Petroleum Directorate 2014; Sundal et al. 2016).

Norway has been a frontrunner in dedicated geological storage, meaning the injected  $\text{CO}_2$  is not used to enhance oil recovery (EOR), but injected with the sole purpose to reduce greenhouse gas emissions to the atmosphere (Global CCS Institute 2020), and avoid carbon taxes. Two large-scale operating  $\text{CO}_2$  storage projects exist in Norway, that gather experience and have build trust in the technique over the last 25 years (Eiken et al. 2011; Ringrose 2020).

Safe, long-term  $\text{CO}_2$  storage is dependent on a range of geological parameters,

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both structural and sedimentological (Bachu 2000; Bachu et al. 2007). For a site to be suitable, the storage reservoir provides thermodynamic conditions such that the  $\text{CO}_2$  can be stored in liquid or supercritical state (Bachu 2000). The critical point of  $\text{CO}_2$  is at  $304,13\text{ K}$  and  $7.38\text{ MPa}$  which is typically reached at a depth below  $700 - 800\text{ m}$  below the surface (Bachu 2000). Permeability and porosity of the constituents of a storage site are crucial for the suitability of  $\text{CO}_2$  storage (Bachu 2015). A storage reservoir should hold the desired amounts of  $\text{CO}_2$  and facilitate distribution of the  $\text{CO}_2$  plume. Further the caprock, a low permeable formation above the storage formation, has to be sufficiently tight (Bachu 2000) and the local faults and fractures have to withstand changes in the stress field (Miocic et al. 2020; Shukla et al. 2010).

The geological complexity and limited data and accessibility of storage sites leave uncertainties connected to the behaviour of the injected  $\text{CO}_2$  and the interaction with the systems rocks and fluids. The uncertainties and known man-made infrastructure or geological features could make for several leakage scenarios as shown in Fig. 1.1 during storage, despite diligent site characterization. The leakage likelihood or rates are, however, estimated to be very low both from modelling (Alcalde et al. 2018) and from studies of natural analogues (Kampman et al. 2016; Miocic et al. 2019).

The leakage pathways may facilitate  $\text{CO}_2$  migration of varying rates, at different locations and on different timescales. On the one hand an injection well leakage could occur immediately after injection and with a high rate, on the other hand  $\text{CO}_2$  may reach an abandoned well after decades or centuries (Fig. 1.1). A way to reduce risk is to pursue offshore storage, as is predominantly done in Norway. This avoids potential contamination of freshwater resources and limits exposure of leaking  $\text{CO}_2$  for humans, thereby increasing public acceptance. Leaking  $\text{CO}_2$  would further not be fed back directly into the atmosphere but would, at least temporarily, dissolve in the ocean. Still, also the marine environment should not be contaminated, however, on the large scale ocean acidification through  $\text{CO}_2$  leakages is estimated to be low (van der Zwaan et al. 2016) and even a local hypersaline brine release is likely to have a small environmental impact due to rapid hydrodynamic dispersion (Blackford et al. 2021).

A measurement, monitoring and verification (MMV) strategy is a part of each large scale storage project to address the leakage scenarios (IEAGHG 2020; Ringrose 2020). If irregularities are observed through the monitoring, a  $\text{CO}_2$  injection strategy can be adapted or injection could even be terminated. MMV accompanying injection informs on the behaviour of the stored  $\text{CO}_2$  and ultimately it allows to verify that the  $\text{CO}_2$  is stored long-term. Thereby, a robust MMV strategy helps to ensure long-term storage security and that the  $\text{CO}_2$  is taken out of the atmosphere long-term.

Besides the scientific suitability of different monitoring techniques, there are economic and societal dimensions of MMV strategies that may contribute towards scaling CCS to climate relevant amounts. On the one hand, the associated cost of such a strategy cannot jeopardize the economic viability of a project which is currently heavily dependent on effective implementation of carbon pricing



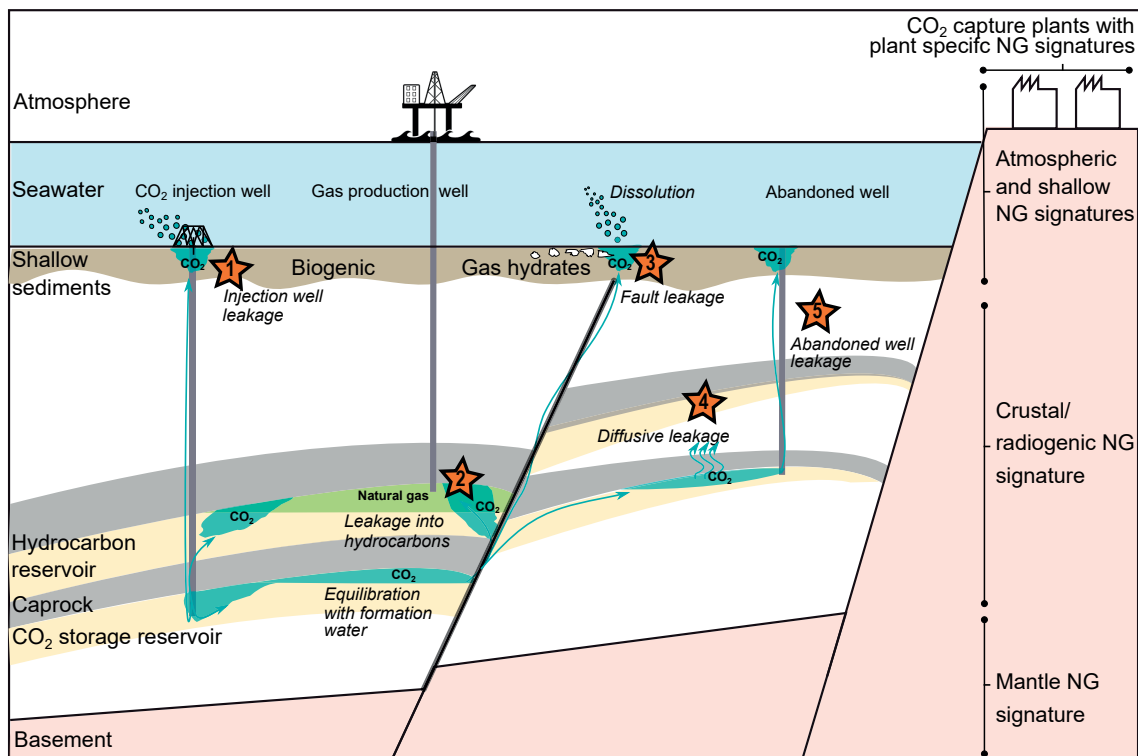


Figure 1.1: Overview of potential leakage pathways of a CO<sub>2</sub> storage site. On the right side areas are marked with typical noble gas signatures, the specific composition of noble gas concentrations and isotopic ratios (Burnard 2013). CO<sub>2</sub> will have different noble gas signatures for different capture plant types, such as post-combustion, natural gas processing or oxyfuel (Flude et al. 2017). Possible leakage pathways are: (1) injection well leakage, (2) migration into and contamination of hydrocarbon reservoirs, (3) fault leakage, (4) diffusive leakage and (5) leakage through an abandoned well. Leaking CO<sub>2</sub> may enter the atmosphere or dissolve in seawater. Figure modified from Paper III.

or subsidies (Hongo 2019). On the other hand, the legal framework regarding long-term liability of safe containment will determine the duration and extent of a MMV strategy (Faure et al. 2017). Further, increased MMV expenditures could improve the environmental reputation of the involved entities (Falcone 2020) and support public acceptance (IEAGHG 2020). However, the latter point is not a certainty and at least one study found that being educated on CCS monitoring did actually not have a reassuring effect (L'Orange Seigo et al. 2011).

From a scientific standpoint monitoring for leakages and unwanted migration, may it be to the surface or in the subsurface can be divided into two areas: leakage detection, i.e. observing a CO<sub>2</sub> anomaly, and leakage attribution, i.e. identifying the source of such an anomaly. There is a variety of techniques, geochemical, geophysical, active and passive that may be included into an MMV strategy (IEAGHG 2020). Gas release in the offshore environment allows for a visual and acoustic detection (IEAGHG 2015). However, it also limits accessibility, for

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example for sampling, and may require the utilization of ships or underwater vehicles (IEAGHG 2015). Several offshore CO<sub>2</sub> release research projects showed that leakages with small rates can be detected on large scales and environmental impact was found to be limited (Dean et al. 2020).

Three prominent and large-scale examples of successful monitoring are presented subsequently. The first one is the seismic surveys conducted at the Sleipner storage site (Chadwick et al. 2010; Chadwick et al. 2005; Furre et al. 2014). Repeated seismic imaging of the CO<sub>2</sub> storage site allowed to depict the development of the distribution of the injected CO<sub>2</sub> plume. This allowed to verify the containment of CO<sub>2</sub>, to history match injection models and to describe the heterogeneity of the storage formation.

The second one is injection well pressure monitoring. Since it is a continuous measurement it has more practical implications than seismic imaging, which may only be performed in intervals of several years. Monitoring the pressure response of a reservoir to injection can validate the permeability and the connectivity of a reservoir. An increase in pressure would be a sign that the formation does not have the necessary storage properties and could ultimately lead to the halt of injection to avoid pressure build-up that would reach levels where fault reactivation could allow for leakages or induce seismicity (Rutqvist et al. 2015). An observation of pressure build-up was the cause to change change of the storage formation at Snøhvit (Hansen et al. 2013).

The third one, is the another large scale dedicated storage site called In-Salah in Algeria. High-frequency satellite imaging, ‘InSAR’, showed surface displacement of centimeter scale above the injection well (Vasco et al. 2008; Vasco et al. 2010), despite the storage reservoir being at 1700 m depth. This observation and the subsequent targeted monitoring techniques raised concerns about a possible leakage which finally lead to the complete stop of CO<sub>2</sub> injection at the site, even though there is no indication that CO<sub>2</sub> has left the confinement zone (White et al. 2014).

The monitoring option that is the focal point of this thesis is a geochemical one, explicitly, the application of noble gas tracers, helium (He), neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe). Noble gases are trace constituents of all environmental fluids as well as the injected CO<sub>2</sub>. Therefore, they have the potential to be tracers that do not have to be added artificially in contrast to more conventional tracers such radioisotopes or fluorocarbon compounds (Roberts, Gilfillan, et al. 2017). Noble gases are also non-toxic and inert. Consequently, their functionality is not compromised by chemical reactions which could be the case for the stable isotopes of CO<sub>2</sub>, <sup>13</sup>C and <sup>18</sup>O (Mayer et al. 2015; Roberts, Gilfillan, et al. 2017).

Noble gases have already proven their usefulness at a large scale storage site. Noble gases were used for leakage attribution when a leakage into a shallow aquifer from the nearby Weyburn-Midale onshore storage site in North America was alleged. The leakage was refuted by using noble gas concentrations and isotopic ratios, the ‘signature’, to exclude that a fluid with the signature of the CO<sub>2</sub> or other hydrocarbons could have contributed significantly at the sampling site (Gilfillan et al. 2017). Further, in CO<sub>2</sub> injection for enhanced oil recovery

(EOR), changes in the noble gas signature of the produced fluids allowed to quantify the contribution of the injected CO<sub>2</sub> (Györe et al. 2017; Györe et al. 2015; Nimz et al. 2005).

Besides the inherent noble gases it has also been discussed to label the injected CO<sub>2</sub> with addition of noble gases to distinguish the noble gas signature of the injected CO<sub>2</sub> further (Nimz et al. 2005; Roberts, Gilfillan, et al. 2017). This has not been conducted at large-scale storage sites and the experience is therefore somewhat limited. Smaller scale experiments, however, allowed identification of the CO<sub>2</sub> gas plume distribution and identifying mixing and degassing processes (e.g. Ju et al. 2020; Lu et al. 2012).

There are uncertainties connected with utilizing noble gases as monitoring tracers. Three main topics need to be addressed: (1) measurement techniques need to be available and sufficient, (2) the background concentrations of the different fluid types of a storage site need to be characterized and (3) the behaviour of the CO<sub>2</sub>-noble gas system needs to be known. These topics shall be addressed in more detail as described in the specific research objectives of this thesis, which will be outlined in the next section. The findings aim to theoretically advance noble gas research but also have a practical application. Thereby, they may become of use for the design of MMV strategies of CCS projects such as the ‘Longship’ project, which is currently under development (Furre et al. 2020).

## 1.2 Research Objectives

### 1.2.1 Measurement Technology

The application of noble gases as geochemical tracers is based on the chemically inert behaviour of these elements (Burnard 2013). The calculation of the processes they undergo is simplified since chemical reactions can be excluded. Often it is reasonable to assume that the noble gas concentrations and isotopic ratios of a fluid are derived from one or several end-members that may be unknown. Therefore, their utilization for understanding fluid flows is heavily dependent on collecting representative samples, including the end-members, and measuring them precisely and accurately. To retrieve these samples, one has to be able to access the right locations at the right time and to extract processable amounts of water or gas from a sample.

The number of samples that are processed and measured is rather limited, despite advances in extraction methods of fluid samples, for example for sediment pore-waters and stalagmites (Brennwald et al. 2013). The limitation derives from the economic and time expenses the analysis of these samples are accompanied with (Popp et al. 2021). In the last decade, this limitation has been reduced by the development of field-deployable mass spectrometers (Brennwald et al. 2016; Chatton et al. 2016; Mächler et al. 2014). These relatively low cost systems can analyse on-site and more frequently than lab-based mass spectrometers. Water streams can even be measured semi-continuously with membrane inlets. Thereby, the amount and extent of noble gas datasets can be scaled up and

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the expenses reduced. Also, the higher frequency of analyses allows to address temporal changes of an environmental system with higher resolution. The continuous measurements also allow the pre-selection of samples for subsequent measurements in the laboratory if higher precision is desired.

The field-deployable systems typically have the drawback of having higher detection limit and allow analysis of fewer isotopes than the lab-based mass spectrometers (Popp et al. 2021). This is mainly caused by leaving out purification steps completely or in parts since they would require for example liquid nitrogen or dry ice (further details in Sec. 1.3.1). This causes higher detection limits and reduces the number of measurable noble gas isotopes, since spectral overlaps are not excluded. A further disadvantage of the field measurements is that especially for continuous measurements with membrane inlets large water volumes, i.e. a high flow rate, is required.

This thesis summarizes different innovative approaches to apply such portable mass spectrometers in CCS. The possible applications can be targeting systems throughout the CCS chain, monitoring and describing the CO<sub>2</sub> capture process, the collection of background signatures and in MMV strategies of storage sites or during injection experiments.

### 1.2.2 Background Signatures

The concentrations and the isotopic ratios of noble gases constitute the noble gas signature of a fluid. This practically labels most environmental reservoirs with an identifiable fingerprint. In the environment three main signatures can be found that are of atmospheric (Sano et al. 2013), crustal (radiogenic) (Ballentine et al. 2002) or mantle (Moreira et al. 2013) type (Burnard 2013). In practice, concentrations and ratios can vary significantly within those main signatures. For example, natural gas typically displays a radiogenic signature, however, the concentrations of a specific isotope can cover several orders of magnitude (Prinzhofer 2013).

The attribution of a CO<sub>2</sub> leakage based on noble gases is conducted by characterizing the observable signatures and then conducting an end-member mixing analysis for a collected sample of the supposedly leaking fluid. This was successfully applied at the large scale CO<sub>2</sub> storage site where an alleged leakage was refuted (Gilfillan et al. 2017). Figure 1.2, taken from Gilfillan et al. 2017, shows an example from the Weyburn EOR project where it was claimed a leakage had occurred. The isotopic ratio <sup>3</sup>He/<sup>4</sup>He is plotted against the <sup>4</sup>He concentration and mixing calculations are performed. Possible CO<sub>2</sub> containing noble gas end-members are of shallow groundwater with an atmospheric signature, injected CO<sub>2</sub> with low <sup>4</sup>He concentrations and the CO<sub>2</sub> produced through the EOR activities (Fig. 1.2). Through the mixing calculations a major contribution of injected or produced CO<sub>2</sub> could be ruled out.

With regards to background fluid characterisation in the North Sea, there are noble gas analyses from two natural gas and oil fields in the North Sea (Ballentine et al. 1996; Barry et al. 2016), which may be suitable analogues for other sites. The samples show significant variation within one gas field. Sediment samples

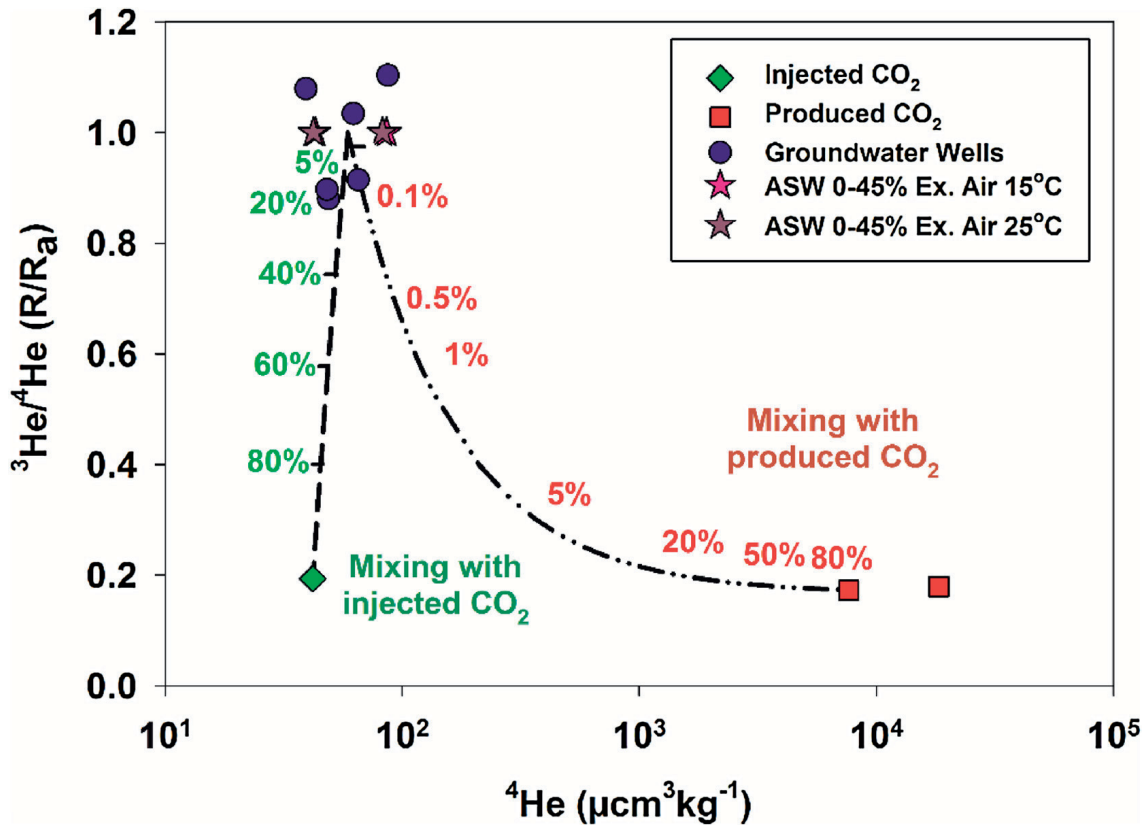


Figure 1.2: Example of an end-member mixing analysis at the Weyburn EOR project using  $^4\text{He}$  and  $^3\text{He}/^4\text{He}$ . The differences in either concentrations or the isotopic ratio allow to rule out a major contribution of the  $\text{CO}_2$  from the EOR activities. Figure from Gilfillan et al. 2017.

from the seafloor have been collected at different locations, which showed a range of values for different geological settings (Horstmann et al. 2021; Nuzzo et al. 2019; Tomonaga et al. 2013). However, none of the settings had similar geological configuration as the North Sea, i.e. they were at plate boundaries and not on continental shelf. Therefore, hardly represent suitable analogues.

Captured, and subsequently injected,  $\text{CO}_2$  has an inherent noble gas signature (Flude et al. 2017). The  $\text{CO}_2$  may stem from various capture plants and processes resulting in a range of noble gas signatures (Flude et al. 2017). The study by Flude et al. 2017 showed that the signature of captured  $\text{CO}_2$  is typically characterised by low concentrations. However, variations on several orders of magnitude and different isotopic ratios for the different capture plants were observed (Flude et al. 2017). For example, plants capturing  $\text{CO}_2$  from oxyfuel combustion were significantly enriched in the heavy noble gases Xe and Kr (Flude et al. 2017). From this study, it is not evident that noble gases in a single sample are representative of the overall noble gas signature in a  $\text{CO}_2$  capture stream. Addressing potential temporal variation was identified as the first application of the portable mass spectrometers.

In summary, the need to characterize both the background signatures of

potential storage locations and of CO<sub>2</sub> from Norwegian CO<sub>2</sub> capture plants can be identified. Therefore, the presented thesis aimed at providing a baseline dataset for the Norwegian offshore storage projects.

### 1.2.3 Fundamental Behaviour of Noble Gas Tracers

The samples and noble gas signatures collected throughout this study were applied in scenarios to estimate applicability of noble gases for CO<sub>2</sub> leakage detection and attribution. To align gas concentrations in the different phases Henry's law can be used (e.g. Kipfer et al. 2002), which links gas and dissolved phases through gas-specific Henry constants. In cases of high CO<sub>2</sub> concentrations, Henry constants for a CO<sub>2</sub>-H<sub>2</sub>O-system need to be included. These were only rather recently derived by Warr et al. 2015.

It is also a possibility to deliberately add noble gases as tracers to the injection stream to distinguish the signature of the injected CO<sub>2</sub> (Nimz et al. 2005; Roberts, Gilfillan, et al. 2017). The estimations of tracer amounts needed and associated costs have not yet included the variability found in background noble gas signatures, the analytical uncertainty as well as the specific phase partitioning between the injected CO<sub>2</sub> and the formation water. Therefore, the calculations were updated in the presented work to validate if the cost for such a tracer addition derived in Nimz et al. 2005 and Roberts, Gilfillan, et al. 2017 still holds true.

Not all the fundamental behaviour of CO<sub>2</sub> and noble gases in the storage reservoir and the caprock is known, despite successful application of noble gas tracers on large scale. Since the likelihood for CO<sub>2</sub> leakages is so low there is limited experience from large scale CCS related leakages. For example, no offshore leakage case has been documented. Therefore, small scale injection experiments have been performed in the past, where simultaneous injection of noble gases allowed identification of the CO<sub>2</sub> gas plume distribution and identifying mixing and degassing processes of the CO<sub>2</sub> both onshore (Ju et al. 2020; Lu et al. 2012) and offshore (Dean et al. 2020).

Fundamentally, injection experiments shall evaluate the behaviour of CO<sub>2</sub> and if the noble gases follow the theoretical description. For example, one property attributed to the noble gases Xe and Kr is that they could have an early warning function (Carrigan et al. 1996; Kilgallon et al. 2018). Noble gases were found to migrate faster than CO<sub>2</sub> and an observed increase in concentrations could initiate a stop of injection or the evacuation of an area to avoid damages prior to CO<sub>2</sub> leakage. Exactly such observational differences, i.e. varying breakthrough times, between noble gases and CO<sub>2</sub> give insight into the additional processes CO<sub>2</sub> undergoes during migration, such as adsorption or precipitation of minerals.

Another aim of this work is therefore to investigate the behaviour of CO<sub>2</sub>-noble gas systems during injection experiments. The high resolution measurements with the portable mass spectrometer shall enhance the application of noble gases for the monitoring of such experiments. The technical experiences gathered may subsequently find use at large scale storage site monitoring.

## 1.3 Methodology

### 1.3.1 Primary Methods

This thesis is based on experimental work, i.e. field campaigns, fluid sampling and laboratory analysis. As described the goal is to show the usefulness of high-frequency measurements with a portable mass spectrometer. Specifically, a miniRUEDI was acquired for this work, which was developed by project partners of ICO<sub>2</sub>P at the Swiss Institute for Aquatic Research (Eawag) (Brennwald et al. 2016). The gas-equilibrium membrane inlet mass spectrometer (GE-MIMS) has primarily been developed for aquatic research, where a number of scientific contributions have already been made, as reviewed in Popp et al. 2021.

The mass spectrometers technical setup is shown in Fig. 1.3[a] and allows comparison to the stationary mass spectrometer which was used when higher precision and accuracy was desired (Fig. 1.3[b]). The membrane inlet separates the dissolved gases of a water stream to a gas head space which can then be sampled (Fig. 1.3). This inlet setup is not mandatory and measurement of a gas stream can be performed as well. Gas ions are then produced with electrons from a heated filament. The ions are then filtered on their mass-charge ratio in a quadrupole field (Brennwald et al. 2020). Neither cold traps, using the different freezing points of gas species, nor zeolite traps are used to separate gas species to analyse them individually. Since the complete gas content of a sample is analysed, the portable mass spectrometer has the advantage to quantify noble gases and major gas species such as N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> simultaneously (Brennwald et al. 2016). Stationary systems are typically specialized on exclusive noble gas measurements.

Complementary to the in-situ analysis with the portable mass spectrometer, fluid samples were analysed with the mass spectrometer in the noble gas laboratory at ETH Zurich, Switzerland. The magnetic sector mass spectrometer in this facility reaches a typical precision of  $\pm 1\%$  as cryogenics are used to select the respective masses (Beyerle et al. 2000 and Fig. 1.3[b]). With the stationary mass spectrometer, less abundant isotopes like <sup>3</sup>He and a wider range of noble gases compared to the on-site mass spectrometry, specifically Ne and Xe, can be quantified. Recently, improved compensation of the spectral overlaps lead to increased accuracy for the measurement of several gas species with the miniRUEDI (Brennwald et al. 2020).

### 1.3.2 Fieldwork

The application of noble gases as geochemical tracers is based on the different noble gas signatures that are found in nature. Therefore, to enable prediction of the suitability of noble gases as monitoring tracers, it is essential to characterize and describe different sites and locations at varying times.

The foundation of the presented work are the fluid samples collected and field experiments performed throughout this study. An overview of most of the sampling and fieldwork locations is given in Fig. 1.4. Impressions of that field

## 1. Introduction

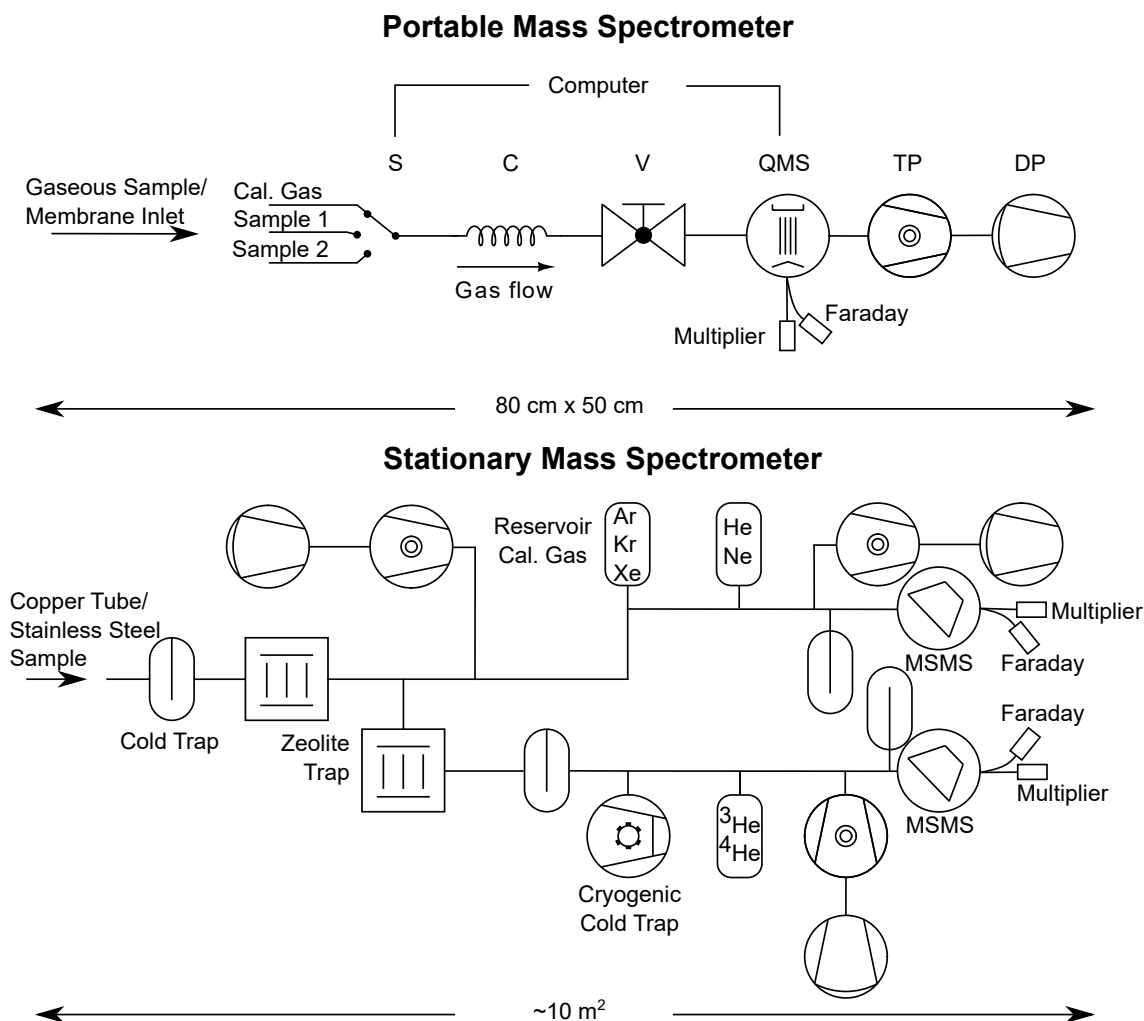


Figure 1.3: Set-up and scale comparison of the portable and stationary mass spectrometers. [a] The portable mass spectrometer with a sampling stream being continuously connected, either as a gas stream or with a membrane inlet module (GE-MIMS-APP, pat. pending), 6-port inlet selector valve (S), quadrupole mass spectrometer (QMS), turbomolecular pump (TP), and diaphragm pump (DP), modified from Brennwald et al. 2016. [b] Lab-based mass spectrometer (simplified to essential parts). Magnetic sector mass spectrometer (MSMS). Cold and zeolite traps are used to separate heavy and light noble gases. Magnets are used to separate isotopes species from each other, after Beyerle et al. 2000.

work are shown in Fig. 1.5. Some minor trial measurements are not included such as measurements close to the North Cape (Fig. 1.5[a]). Some analyses of samples are still being conducted or results are being processed. However, each sampling campaign and participation in experiments delivers valuable experiences that are a part of the work presented. Therefore, they are included in the following description which also relates the fieldworks to the respective publications or manuscripts.

Prior to this PhD project, in 2017, noble gas data was collected to apply the



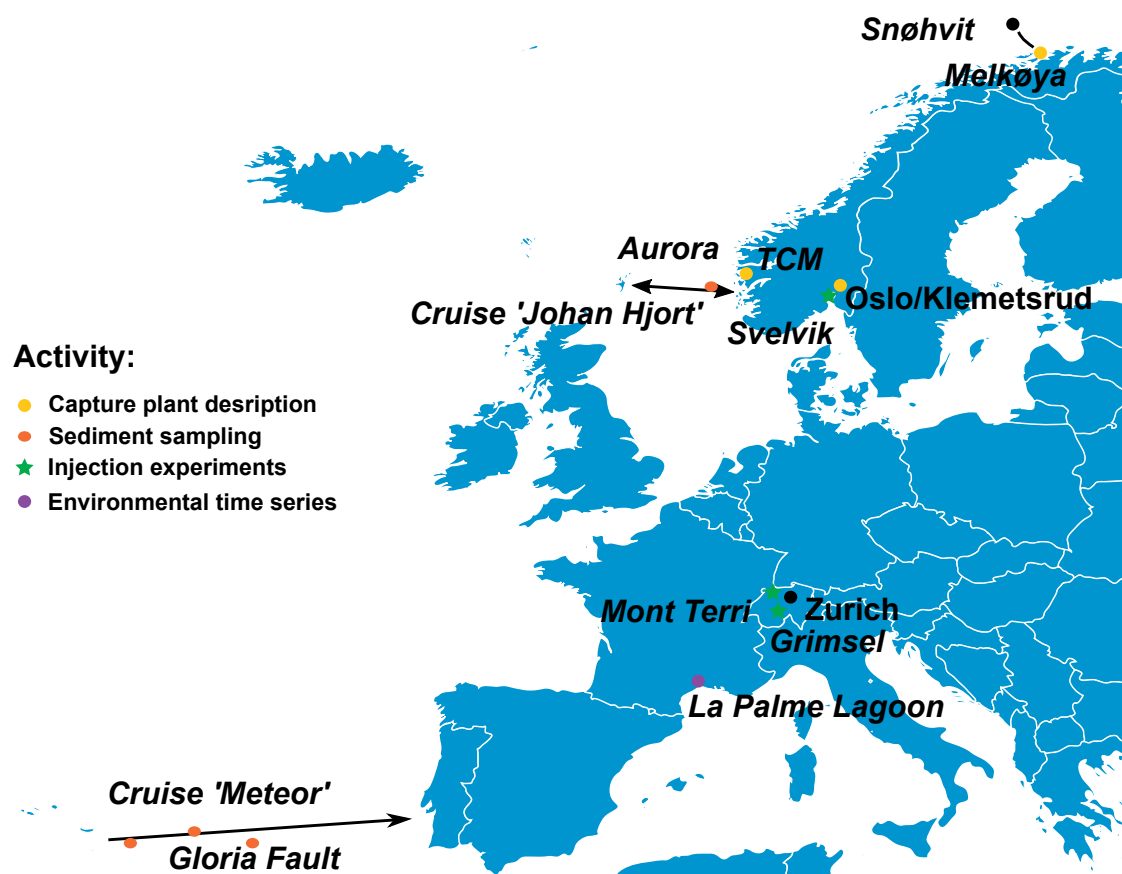


Figure 1.4: Overview of the locations where fieldwork was performed: CO<sub>2</sub> capture sites Technology Centre Mongstad (TCM), Melkøya and Klemetsrud. Field experiments at Mont Terri, Svelvik, the La Palme Lagoon and Grimsel. Research cruises for seafloor sediment sampling from the Azores to Portugal on ‘RV Meteor’ and from Bergen to the Shetland Islands and back on ‘RV Johan Hjort’ both in 2020.

portable mass spectrometer on air-water gas exchange quantification during a field study at La Palme Lagoon at the Mediterranean Sea in France. Essential parts of the analysis and the publication of the results was conducted within the PhD. The results are presented in Paper I. The work demonstrates the applicability of the miniRUEDI mass spectrometer to solubility changes, which is highly relevant for the application in CO<sub>2</sub> capture processes and inspired the subsequent field campaigns at the Technology Centre Mongstad (TCM).

A feasibility study with the portable mass spectrometer at TCM, a CO<sub>2</sub> capture research facility, provided a transition to the application in CCS. The results of the study that had also been conducted in 2017 were analysed during the PhD and published in a conference paper (Pap. A.1). The successful trial led to several further sampling campaigns at TCM. In total 4 weeks of on-site analysis of the gas streams were performed at the Technology Centre Mongstad in 2018. At Melkøya, the capture plant in the Snøhvit project, the mass spectrometer was set up in August 2018, but concerns regarding methane leakages at the plant

stopped the on-site measurements. However, single samples at several locations throughout the plant were collected, which allow to define the major effects of the CO<sub>2</sub> absorption process on the noble gases at Melkøya. The samples from the natural gas from the Snøhvit Field, which is processed at the Melkøya plant, also collected during this research stay, are the first hydrocarbon samples from the Barents Sea analysed on the noble gas content. The results from both sites are described in Paper II. As a last site for CO<sub>2</sub> capture, samples were collected at the waste-to-energy plant Klemetsrud, where a capture test facility was installed during 2019. The results are described in a conference paper (Paper A.2).

Then, to address the background noble gas concentrations at potential storage sites two research cruises were conducted. Sampling for noble gases in the pore-water of the sediments was conducted after the method described in Brennwald et al. 2003. The first cruise was organised by the GEOMAR Helmholtz Centre for Ocean Research in Kiel. The six weeks on the German research vessel ‘Meteor’ between the Azores and Portugal in spring 2020, served as training for a two week research cruise in the North Sea with the ‘Johan Hjort’ in late summer 2020 (Fig. 1.5[b]). The ‘Meteor’ cruise targeted the plate boundary between Africa and Eurasia, the Gloria Fault and aimed at identifying fluid flow from the fault (Cruise report: Hensen et al. 2020). The ‘Johan Hjort’ cruise was arranged by the Norwegian Institute of Marine Research (HI). Besides their primary objective of measuring fish population, I was provided with the possibility to sample the seafloor above the Aurora area and the Troll oil and gas field, the current storage prospect area of the ‘Longship’ project (Norwegian Ministry of Petroleum and Energy 2020). The sediment samples of the second cruise were complemented with natural gas samples from several production areas of the Troll oil and gas field organized in cooperation with Equinor. Despite the COVID-19 pandemic, it was possible to conduct these research cruises. However, increasing case numbers introduced heavier travel restrictions and laboratory closures, such that the results were not ready within the scheduled completion time of this doctoral degree. These samples are currently being processed, and results will be published as soon as possible (see also Outlook, Sec. 3.3).

Two injection experiments were taken part in. The first one was at the ECCSEL Svelvik CO<sub>2</sub> Field Lab (Sintef 2021). The laboratory is located in a sand quarry and the siliciclastic sediments may be considered a shallow storage reservoir analogue. Four new monitoring wells of 103 m depth were installed around an existing injection well and the ICO<sub>2</sub>P project took part in the geological description of the well bores. The following injection experiment was conducted with noble gas tracer addition (Weber et al. 2020), but experienced a partial injection well leakage. Quantification measurements of the leakage were obtained in cooperation with GFZ Potsdam, Germany. However, the data has not yet been published. The initial goal of the detection of different breakthrough time of noble gas tracers and the CO<sub>2</sub> by continuous monitoring with the mass spectrometer was not achieved.

The second injection experiment, called ‘Carbon Sequestration - Series D (CS-D)’ an ELEGANCY-ACT project, was conducted in the Mont Terri Rock Laboratory. Here, based on the experiences with the miniRUEDI, I was invited

to process the geochemical monitoring data of an injection into the Opalinus Clay. The formation is a caprock analogue due to its low permeability (Bossart et al. 2017). Results of the installation phase of the site can be found in Zappone et al. 2021 and Wenning et al. 2021. After installation, an injection with CO<sub>2</sub> saturated water below fault activation pressure was conducted from June 2019 to August 2020. The results of the geochemical monitoring during that time period are presented in Paper IV. Due to travel restrictions prolonged fieldwork and laboratory analysis by myself was, however, prohibited.

The sampling set-up of the portable mass spectrometer that was used during the experiment was inspired from fieldwork prior to this PhD. In the Grimsel Test Site (Fig. 1.5[c]), another Suisse rock laboratory, a hydraulic fracturing experiment was monitored (Roques et al. 2020). Since it provides insights into noble gas release during such events it is a highly relevant supplement to the results of this PhD. Since parts of the analysis and the publication were conducted during the PhD, the paper is included in the appendix in Paper B.1.



Figure 1.5: Impressions from the field work. [a] Test measurements with the miniRUEDI at the North Cape. [b] Measurements and sampling during the ‘Johan Hjort’ cruise in the North Sea. Seafloor water sampled with the CTD in the background analysed with the miniRUEDI in the front. Sediment core sampler in the center. [c] Sampling and measurements with the miniRUEDI at the rock laboratory Grimsel.



# Chapter 2

## Results

### 2.1 Paper I: A Novel Approach to Quantify Air–Water Gas Exchange in Shallow Surface Waters Using High-Resolution Time Series of Dissolved Atmospheric Gases

**Metadata** U. W. Weber, P. G. Cook, M. S. Brennwald, R. Kipfer and T. C. Stieglitz. Published in: *Environmental Science & Technology*, 2019, volume 53, issue 3, pp. 1463–1470. DOI: 10.1021/acs.est.8b05318.

**Motivation and Objectives** Gas exchange across the air-water interface is a key process determining the release and uptake of greenhouse gases from surface waters, and a fundamental component of gas dynamics in aquatic systems. Experimental quantification of the local gas transfer velocity in a wide range of aquatic settings is labour intensive and typically requires the addition of an artificial gas spike. Therefore, we applied a field-portable mass spectrometer for the in-situ, near-continuous measurement of dissolved (noble) gases to develop a novel method, that utilizes only natural, i.e. temperature-induced, variations in dissolved gas concentrations.

**Method and Procedure** The method is based on the fundamental idea that dissolved gas concentrations do not instantaneously follow a change of the equilibrium concentrations stemming from solubility changes. The occurring concentration gradients are equilibrated through diffusion, described by Fick's law. The time of equilibration is dependent on water depth and the local gas transfer velocity ( $k_i$ ).

In practice, dissolved concentrations are measured with the GE-MIMS and the equilibrium concentrations for the given temperature and salinity conditions are derived from Henry's law. Then Fick's law is fitted to the experimentally measured gas concentrations to derive the gas transfer velocity from the amplitude and the phase lag between observed and equilibrium concentrations.

**Key Findings** The method proved successful for determining the local gas transfer velocity. With the current experimental setup, the method is sensitive to gas transfer velocities of  $0.05 - 9 \text{ m/d}$  (for  $N_2$ ), at a water depth of  $1 \text{ m}$ , and a given daily water temperature variation of  $10^\circ\text{C}$ . The range of transfer velocities that can be determined is limited by two factors. On the one hand, the lower limit is caused by the transfer velocity being too low to change the dissolved, in-situ concentrations significantly enough to be detected by the mass spectrometer.

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On the other hand, the upper limit is caused by the transfer velocity being so large that the lag between in-situ concentrations and equilibrium concentrations cannot be resolved anymore.

In a field study in a shallow coastal lagoon different weather conditions allowed the observation of a range of transfer velocities, demonstrating the field applicability of the method. The changes in the transfer velocity were linked to different wind conditions which is an important driver for gas transfer by inducing turbulence in the water to move water bodies to the surface that still have a high concentration gradient towards the air.

The method increases local and temporal resolution with which gas transfer velocity can be determined. The method developed here, thus has the potential to greatly improve on the ability to measure air-water exchange in shallow waters. Improvements of experimental equipment will increase the measurable range and decrease necessary temperature changes

Gas transfer velocities will also determine how fast a CO<sub>2</sub> leakage released to the ocean reaches the atmosphere. However, for deeper parts of the ocean, the surface transfer velocity plays a minor role. Temperature stratification of the ocean, ocean currents and deep circulations are of greater importance. Still, since a leak could occur in gaseous form, the CO<sub>2</sub> may reach much shallower depths before being completely dissolved in the water.

The study proved that the mass spectrometer is capable to derive mass balance parameters from solubility changes. This finding motivated the application to the absorption process by amine gas treatment, since also here a gas phase is dissolving into a liquid phase.

### 2.2 Paper II: Noble Gases in Gas Streams at Norwegian CO<sub>2</sub> Capture Plants

**Metadata** U. W. Weber, R. Kipfer, E. Horstmann, P. Ringrose, N. Kampman, Y. Tomonaga, M.S. Brennwald and A. Sundal. Published in: International Journal of Greenhouse Gas Control, 2021, Vol. 106, DOI: 10.1016/j.ijggc.2020.103238.

**Motivation and Objectives** Flude et al. 2017 have shown that captured CO<sub>2</sub> typically has low noble gas concentrations, however, each CO<sub>2</sub> capture site can have very individual noble gas concentrations and isotopic ratios. Therefore, this paper targeted to characterize the Norwegian large scale capture sites, i.e. the Technology Center Mongstad (TCM) and Melkøya, the industrial complex belonging to the Snøhvit CCS project. The plant type, i.e. natural gas processing, at Melkøya had further not been characterized at all.

From the previous studies it is also not evident that noble gases in a single sample from a CO<sub>2</sub> capture streams are representative of the overall noble gas signature, due to potential temporal variation. After having conducted a feasibility study at TCM (Pap. A.1), that proved installation of the on-site measurements and gave first indications for temporal variation, we aimed to monitor the gas streams for a longer time period.

The measurements shall allow to define the factors controlling noble gas concentrations in captured CO<sub>2</sub>, to monitor temporal variation of noble gas concentrations and finally evaluate the potential to use noble gases as inherent environmental tracers for labelling CO<sub>2</sub> in storage reservoirs.

**Method and Procedure** In total three sampling campaigns at the two CO<sub>2</sub> capture plants were conducted. At both sites, CO<sub>2</sub> is captured using amine gas treatment, i.e. the flue gas from which the CO<sub>2</sub> is captured is brought into contact with an aqueous amine solvent in the absorber. The reacting and dissolving CO<sub>2</sub> is subsequently exsolved by heating the amine solvent in the stripper resulting in a highly concentrated CO<sub>2</sub> gas stream. For the characterization of the capture process the dataset combines time series of in-line sampling with discrete gas sample analysis using a lab-based mass spectrometer with higher analytical precision.

At TCM, a sampling point of the flue gas, from which CO<sub>2</sub> was captured, and one of the CO<sub>2</sub> product streams were simultaneously analysed. A calibration gas was produced to mimic CO<sub>2</sub> streams, since in default settings the mass spectrometer uses air as calibration gas.

**Key Findings** Noble gas concentrations in the gas streams were observed to decrease by several orders of magnitude during the absorption process. Isotopic ratios are air-like for CO<sub>2</sub> captured after natural gas combustion at TCM since air is used for combustion. The ratios are of radiogenic type, typical for natural gas, for CO<sub>2</sub> captured from natural gas processing on Melkøya. Further, a solubility trend caused by the amine solvent at TCM with higher solubility for heavier noble gases was detected. Currently, however, analysis of the captured CO<sub>2</sub> with the portable mass spectrometer is limited to Ar, due to the generally low concentrations.

It was found that the relative concentrations of noble gases in the captured CO<sub>2</sub> are defined by the gas from which the CO<sub>2</sub> is captured and the design of the amine gas treatment process. For instance the variation of the composition of the combusted fuel at the combined heat and power plant, from which the CO<sub>2</sub> is captured, is observable. Both factors were observed to cause temporal variation in the captured CO<sub>2</sub>.

Mixing and noble gas partitioning calculations were performed based on the phase partitioning data for a high pressure CO<sub>2</sub>-H<sub>2</sub>O-system (Warr et al. 2015). We find that the significant depletion in noble gas concentrations, together with degassing of noble gas enriched formation water into the CO<sub>2</sub>, cause the injected CO<sub>2</sub> to inherit the noble gas signature of the storage formation, even following the injection of significant CO<sub>2</sub> volumes. Any CO<sub>2</sub> leaked from the storage formation is thus likely to have a crustal noble gas signature, characteristic of the storage site, which can be targeted for monitoring.

**Additional Information** After this study, samples were collected at the waste-to-energy plant Klemetsrud. Results can be found in the conference paper in the

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attachment (Pap. A.2). Meanwhile TCM could become a CO<sub>2</sub> contributory to the ‘Longship’ project, Klemetsrud is certainly aimed to be one of the industrial sources (Norwegian Ministry of Petroleum and Energy 2020). The CO<sub>2</sub> captured during a feasibility capture program at Klemetsrud exhibits even lower noble gas concentrations than previously observed (Pap. A.2). This may be caused by the high CO<sub>2</sub> purity achieved or by the progressed degradation of the solvent during sampling, which reduces solubility (Buvik et al. 2021).

### 2.3 Paper III: Techno-Economic Aspects of Noble Gases as Monitoring Tracers

**Metadata** U. W. Weber, N. Kampman and A. Sundal. Published in: *energies*, 2021, Vol. 14, no. 12, DOI: 10.3390/en14123433

**Motivation and Objectives** Papers II and A.2 describe that the injected CO<sub>2</sub> is likely to inherit a radiogenic noble gas signature from the storage formation waters through equilibration or mixing with native formation gases. The calculation based on phase partitioning data for a high pressure CO<sub>2</sub>–H<sub>2</sub>O-system, led to the hypothesis, that injected CO<sub>2</sub> becomes differentiable from atmospheric signatures without the need of adding tracers.

In this work, we aimed to validate the hypothesis of the inherent differentiability quantitatively. These calculations should include current analytical capabilities for noble gas measurements and the natural variability of noble gas signatures observed in background reservoirs. Distinctiveness calculations to other environmental signatures, i.e. natural gas and gas hydrates, were supposed to be included.

Further, the calculations were extended to the addition of noble gas tracers to label the injected CO<sub>2</sub>. This had already been discussed from a practicality and cost perspective for large scale storage in Nimz et al. 2005 and Roberts, Gilfillan, et al. 2017. We included the solubilities from Warr et al. 2015 in these calculations and aimed to analyse the financial impact of such a tracer addition.

**Method and Procedure** We assessed and demonstrated the suitability of noble gases in source identification of CO<sub>2</sub> anomalies even when natural variability and analytical uncertainties are considered. Therefore, we collect plausible baseline datasets for the different background reservoir in the North Sea. Shallow sediment signatures were only available for geological settings not comparable to the North Sea.

We applied a criterion for being distinct aiming to include uncertainties more realistically, thereby varying from previous studies Nimz et al. 2005 and Roberts, Gilfillan, et al. 2017. In explicit, the criterion is that the resulting concentration in a mixture of 90 % background fluid and 10 % equilibrated CO<sub>2</sub> has to be larger than the natural variability plus the  $3\sigma$ -interval of the typical measurement error as stated in Barry et al. 2016.



For the economic calculations for the tracer addition, the same cost for a gas or isotope are used as in Roberts, Gilfillan, et al. 2017. This facilitates comparison between the studies.

**Key Findings** The injected CO<sub>2</sub> becomes distinguishable from shallow fluids due to its inheritance of the radiogenic signature (e.g. high He) of deep crustal fluids by equilibration with the formation water. This equilibration also results in the CO<sub>2</sub> inheriting a distinct Xe concentration and Xe/noble gas elemental ratios, which enables the differentiation from natural gas, that may be in the vicinity of a storage reservoir. The derivation still has uncertainties that may make the latter distinction less reliable. Here, knowledge on solubilities of noble gases in more complex fluid systems may change results. Further, the assumption of full equilibration may not hold true for all cases.

The uncertainties would be best and most economically addressed by co-injection of Xe isotopes into the CO<sub>2</sub> stream. Added concentrations would be low enough not to alter the properties of CO<sub>2</sub>. This general result is in line with calculations from Nimz et al. 2005 and Roberts, Gilfillan, et al. 2017, however, the derived cost differs significantly to the upside in our calculations. A tracer addition, would add significant cost to monitoring programs of currently operating storage projects with up to 70% increase (i.e. from 1 \$US/t to 1.7 \$US/t). This is under current financial schemes of CCS which are largely dependent on CO<sub>2</sub> pricing or taxing schemes likely uneconomical.

**Additional Information** The phase partitioning calculations are dependent on the volume ratio of CO<sub>2</sub> and water. This ratio is constrained by the irreducible water saturation of the reservoir rock hence not all the formation water can be expelled by the injected CO<sub>2</sub>. Papers A.2 and A.3 show an example of the relative concentrations in dependence of the gas-water volume ratio. Up to the irreducible water ratio the gases stripped from the formation water largely dominate the concentrations in the CO<sub>2</sub>. Paper A.3 also depicts the partitioned concentrations in dependency of the gas-water volume ratio for a tracer addition.

In Paper A.2, the CO<sub>2</sub> partitioning calculations were expanded to different depth as thermodynamic conditions change since temperature and pressure are a function of depth. The general result of the stripping from the formation water is maintained throughout the analysed depth profile.

### 2.4 Paper IV: Geochemical Evidence for Cross-Fault CO<sub>2</sub> Migration in a Caprock

**Metadata** U. W. Weber, A. P. Rinaldi, C. Roques, A. Zappone, S. Bernasconi, M. Jaggi, Q. Wenning, S. Schefer, M. Brennwald and R. Kipfer. Unsubmitted manuscript, 2021

**Motivation and Objectives** The sealing characteristics of the formation above a CO<sub>2</sub> storage reservoir, the caprock, is essential to the functioning of geological carbon storage. In case CO<sub>2</sub> were to enter the caprock, temporal changes of the geochemistry can reveal fundamental information on migration mechanisms and induced chemical reactions.

Previous injection experiments on low-permeable rock have largely been limited to small scale laboratory studies (Alemu et al. 2011; Credoz et al. 2009; Kaszuba et al. 2005; Vilarrasa et al. 2017). The Mont Terri Rock Laboratory makes the Opalinus Clay accessible and allows to conduct more realistic experiments (Bossart et al. 2017). The experiment includes a wide-range of monitoring techniques and aims to gain knowledge on the migrational behaviour of CO<sub>2</sub> saturated water in a caprock. The presented work in this thesis focuses on the integration and comparison of several geochemical tracer approaches.

**Method and Procedure** Detailed site characterization prior to the injection experiment resulted in the development of an injection strategy that has a constant injection pressure below fault opening pressure and was aimed to be a year long. The time frame was chosen since a pressure and brine change was modelled, based on estimations of the rocks and fractures permeabilities, to be able to cover the distance between the monitoring and the injection borehole (Zappone et al. 2021).

The geochemical monitoring of the experiment focused on the temporal evolution of dissolved gases, including noble gases, stable isotopes and ion composition. Due to the low flowrates, and the high pressure conditions, the application of the portable mass spectrometer involved the development of a depressurization cycle and was limited to weekly or bi-weekly measurements. The injection water was labelled with a low  $\delta^{13}C$  value compared to the background and Kr was added to the injection water in pulses.

**Key Findings** In total 25 l of water were injected during approximately 14 months. An increase in dissolved CO<sub>2</sub> at the monitoring interval was observed throughout the injection period. However, the increase of the CO<sub>2</sub> could be caused both by the injection and the local pore-water. The confirmation that the injection water was migrating through the fault to the monitoring borehole was a decrease in  $\delta^{13}C$  values.

However, also pore-water was pushed into the monitoring interval revealed by increasing He values. He is naturally enriched in the pore-water due to  $\alpha$ -decay

of radioelements in the rocks. Noble gas concentrations were in a mixing area of atmosphere and previously observed values at the Mont Terri laboratory and depict the distinct phases of the experiment: pore-water being pushed into the monitoring interval, arrival of the injected water and equilibration between the different water types. Sudden changes in the ion composition, explicitly the calcium and magnesium ratio. These changes are not related to first order mixing of the water types indicate phases of dissolution and precipitation.

The first major peak in CO<sub>2</sub> appears after approximately five months. Kr arrives two weeks earlier at the monitoring borehole. The retardation of the CO<sub>2</sub> may be caused by dissolution and precipitation reactions that are induced by the injection. This is evidence for the early warning function of some noble gases, however, analysing this quantitatively had limitations due to the low frequency of the dissolved gas measurements. Overall, there is no evidence for long-term permeability changes, with the flow being bound to the local, small scale fracture network and not the large scale fault structure. Permeability stayed low and the low injected volume reassure the functionality of a caprock with similar composition as the Opalinus Clay.

For large scale monitoring, the carbon added from e.g. CaCO<sub>3</sub> dissolution could affect the tracing functionality of  $\delta^{13}C$ , so to rely on this tracer the signature of the injection water should be significantly different to the background. The formation waters high He concentrations are at first advancing and then mixing with the CO<sub>2</sub> making it a natural tracer in a leakage case. This is in alignment with the theoretical conclusions in Paper II and Paper III. Further, we did not observe a long-term pH decrease at the monitoring borehole. Consequently, pH may not have a critical monitoring character for a CO<sub>2</sub> storage site.

The results also highlight the integrative information gained from including a suite of geochemical tracers into a monitoring strategy since the observed processes were at the current state of the analyses not resolved by geophysical monitoring. Optimisation of membrane modules for high pressures, injection of several noble gases alongside the CO<sub>2</sub> and rock stimulation during the injection are amongst the possible adaptations for future experiments at the Rock Laboratory.



# Chapter 3

## Conclusion and Outlook

### 3.1 Main Findings

The overarching aim of this thesis was to advance knowledge on the behaviour and application of noble gases in the realm of CCS processes and monitoring. This aim was split up into three subjects as detailed in Sec. 1.2: (1) Measurement technology, (2) background characterization and (3) fundamental behaviour of noble gases as tracers.

Chapter 2.1 of this thesis demonstrates the capabilities of semi-continuous on-site (noble) gas measurements by establishing a novel approach to quantify air-water gas exchange at a local scale without the need for tracer injection (Paper I). The temporal differences between in-situ and equilibrium concentrations derived from temperature-induced solubility changes can currently be utilized for the determination of the gas transfer velocity,  $k$ , for shallow water depths with high sensitivity to temperature changes.

Chapter 2.2 shows that the introduction of such highly resolved gas time series into CCS research can further the characterization of background signatures, capture plants and fundamental behaviour through injection experiments. The transfer of on-site mass spectrometry from aquatic, hence atmospheric, science to a CO<sub>2</sub> stream has delivered refined knowledge of the capture systems and the resulting noble gas concentrations by observing temporal variation of noble gases in the captured CO<sub>2</sub> (Paper II). The technology would also allow for screening sites, both capture and storage sites, before deciding if and when high precision samples should be collected, since the portable instrument is currently largely insensitive to the very low concentrations in the captured CO<sub>2</sub>.

The sampling campaigns at the CO<sub>2</sub> capture plants show that noble gas concentrations of captured CO<sub>2</sub> can cover multiple orders of magnitude. The expansion of the database through the studies II and A.2 allows to estimate the signature of future CO<sub>2</sub> sources and make a prediction of temporal variation possible if CO<sub>2</sub> is captured and mixed from several sources. Thereby, decisions can be made if a high frequency monitoring of noble gases is necessary. The temporal variation in the captured CO<sub>2</sub> of one capture plant is, however, likely going to be of minor importance for the monitoring of a storage site due to the mixing with other fluids and the phase partitioning of the injected CO<sub>2</sub> with the formation water which leads to significant gas stripping into the injected CO<sub>2</sub> (Paper III).

The site-specific data-sets included in the thesis prove that each capture site is different and that the history of each geological reservoir results in different noble gas concentrations, i.e. the differences of noble gas concentrations between natural gas samples from the Barents and the North Sea (Paper II). Even

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though, these samples are geographically limited to Norway, the findings are likely to be transferable to sites with similar settings. The sediment samples from the North Sea and gas samples from the Troll Field that were not analysed in their completeness before the preparation of this thesis will strengthen the baseline dataset and are expected to confirm the need for comprehensive baseline characterization. Preliminary results are shown in the outlook (Sec. 3.3).

The modelling of the behaviour of CO<sub>2</sub> after injection, i.e. phase partitioning with formation water shows that an imprint of the CO<sub>2</sub> with high He and Xe concentrations can be expected to be detectable and discriminable against all backgrounds during a number of leakage scenarios (Paper III). This makes inherent noble gas tracers a feasible technique for leakage attribution. Tracer addition, e.g. Xe isotopes, is, in contrast to previous studies, estimated to be too costly at the current financial conditions of CCS since it would increase the total monitoring cost by up to 70 % percent of current levels (Paper III).

Chapter 2.4, demonstrates that the radiogenic accumulation of He in formation water is a natural tracer for formation water and that this signature is ultimately transferred to the injected CO<sub>2</sub>. This is one of the results of the field injection experiments in the low permeable rocks shown in Papers IV and B.1. The uptake of radiogenic He is directly shown to allow for discrimination against atmospheric signatures. Paper IV is a significant step forward for the application of the GE-MIMS technology in a high pressure and low flow environment. Despite the valuable gas data collected, the experiment further demonstrates the benefits of combining several geochemical tracers. In their completeness, dissolved gases, stable isotopes and the ion composition deliver certainty over the small scale migration of the CO<sub>2</sub>-saturated water and the triggering of chemical reactions. It was also observed that pH is, in contrast to the initial expectation, not necessarily decreasing, depending on the mass balances and leakage rates. The experiment shows that the migration is bound to a heterogeneous and disconnected fracture network that prohibits large scale leakage. Further, the low permeability of the caprock formation is not significantly altered, if at all reduced, which is a confirmation of the stability of the caprock.

### 3.2 Recommendations

This research project also aimed at providing suggestions for the monitoring of the upcoming Norwegian CO<sub>2</sub> capture and storage project ‘Longship’. The project plans to inject CO<sub>2</sub> from decentralized industrial sources. Currently, the capture facility at the Brevik cement plant is funded. This specific source of CO<sub>2</sub> has not been characterized on noble gases. However, with the samples analyses provided here it is reasonable to expect low noble gas concentrations with atmospheric isotope ratios if air is used during the combustion process. An initial sampling of the captured CO<sub>2</sub> seem worthwhile, however continuous monitoring are likely of lower importance as long as only one CO<sub>2</sub> source is contributing to the injected CO<sub>2</sub> of the project.

The injected CO<sub>2</sub> will strip noble gases from the storage formation and

adapt a radiogenic signature as shown in Paper III. During migration the CO<sub>2</sub> would be constantly exposed to noble gas rich formation water or other residual gases. This makes for a monitoring target against atmospheric signatures. The calculations also suggest high likelihood for detectability against natural gas, which is contained and produced from reservoirs in the vicinity of the storage site (see Fig. 3.1). The theoretical differentiation towards natural gas may require an experimental proof before relying solely on this approach. Samples of the natural gas from the Troll oil and gas field and seafloor sediment samples have already been collected but are not yet fully analysed. These samples will allow further analysis and provide the missing end-members for this storage site. The foundation for the monitoring utilisation of noble gases will therefore be given.

The planned, continuous MMV program in the ‘Longship’ project currently does not include noble gases (Furre et al. 2020). The content of the triggered environmental monitoring surveys is, however, not yet defined. Given the contribution of noble gases to leakage attribution, their sampling and analysis should be included both during these triggered and routine environmental surveys. Further, some fluid samples that are collected during drilling of wells or environmental surveys may not be reproducible considering that an elaborate sampling setup had to be installed or that costly sampling campaigns/cruises had to be conducted. Therefore, once retrieved, samples should also be analysed for the whole range of geochemical parameters, including noble gases.

The benefits through addition of artificial noble gas tracers, most likely in the form of Xe isotopes, do currently not outweigh the financial drawdown and does therefore not need to be (see Paper III). Assuming the indications of an early warning function of such a tracer can be confirmed, the application may be of increased interest in onshore projects where consequences of a leakage could be more significant.

## 3.3 Outlook

### 3.3.1 Upcoming Samples

Several additional samples were collected and are currently being processed and analysed. This includes seafloor sediment samples which were collected in summer 2020. In total, ten gravity cores with 18 sediment samples were with locations following a trajectory from the EOS well, likely the future CO<sub>2</sub> injection well, towards the Smeaheia CO<sub>2</sub> storage prospect in the east (Fig. 3.1). These sediment cores represent the first ones from the North Sea being analysed on noble gases.

The preliminary results of two cores are currently available. A steep gradient from atmospheric values at the shallowest samples towards natural gas values can be observed for the <sup>3</sup>He/<sup>4</sup>He-ratio in both cores, one nearby the Aurora and one above the Smeaheia alpha storage prospect (Fig. 3.1). The difference in the gradient may be a result of the compaction of the sediments, since more central locations in the Norwegian Channel have lower sedimentation rates (De Haas

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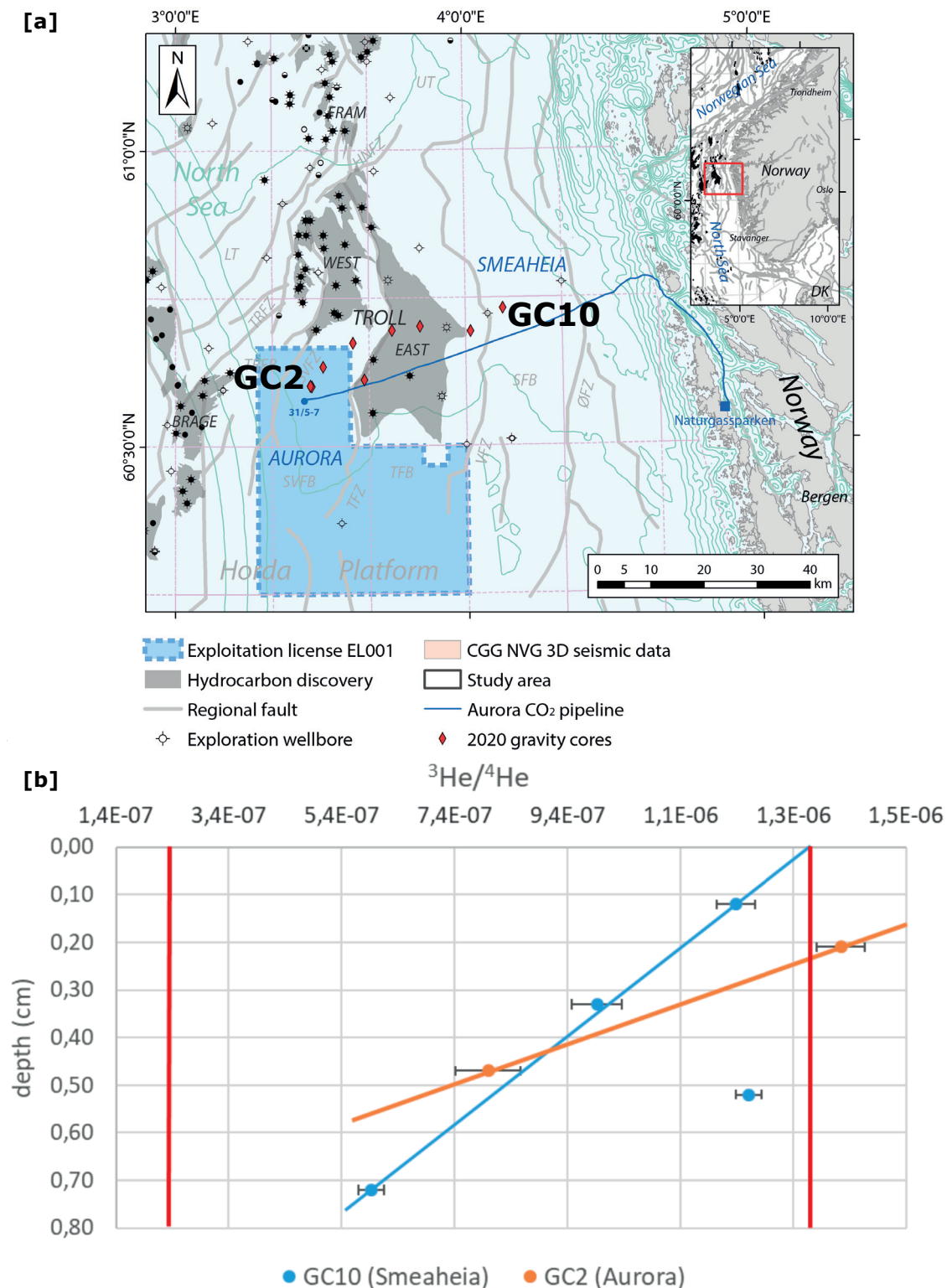


Figure 3.1: [a] Location of the gravity cores (GC) collected in the North Sea at the Aurora storage prospect (labeled as injection well) and the Troll oil and gas field during the research cruise on the ‘Johan Hjort’ (see Fig. 1.4 and Sec. 1.3.2). [b] Preliminary  ${}^3\text{He}/{}^4\text{He}$  concentrations in the pore water of two gravity cores in dependence of depth from the seafloor. Samples were extracted after the method described in Tomonaga et al. 2011 and measured on the stationary mass spectrometer in Fig. 1.3[b].



et al. 1996). The fast decrease in  $^3\text{He}/^4\text{He}$  is likely not achievable through in-situ production considering the sedimentation rates and low accumulation rates.

Further, in June 2021 a total of nine gas samples from several production areas of the Troll field were received, which have not yet been analysed. They will allow evaluation of the charging mechanism of the Troll Field similar to studies on the Magnus Field (Ballentine et al. 1996) and the Sleipner Field (Barry et al. 2016). In the case of the Troll Field the samples are of special interest since the Troll gas field lies in the vicinity of the  $\text{CO}_2$  injection and leaking  $\text{CO}_2$  from below may end up in the Troll gas reservoirs.

Generally, the results from the additional samples will allow to improve the evaluation of detectability of noble gas storage sites conducted in Paper III and increase the scientific significance for offshore settings.

### 3.3.2 Future Research

This study addressed several research questions within the application of noble gas tracers at large and small scale  $\text{CO}_2$  storage sites and capture facilities. Due to the manifold of topics that triggered interest and appeared of high priority, other research ideas or follow-up questions that have come up in the process of the thesis remain unaddressed. The most evident, and in my opinion worthwhile, next steps are detailed below.

- **Injection Modelling:** The leakage modelling in Paper III only includes detailed thermodynamic calculations for the densities of  $\text{CO}_2$  and water at storage reservoir conditions. The densities are in turn used in the phase partitioning calculations which allow the adaptation of Henry's law and performing first order mixing calculations as is common in noble gas research (Burnard 2013).

Mixtures with gases subsequent to injection and changing physical conditions during migration, i.e. temperature and pressure, would, however, change the equilibrium conditions and may lead to phase transitions or other changes of the fluid properties. Also, the brine composition or the rocks mineral assembly of a storage site may influence the thermodynamic conditions and impact storage or migration behaviour.

An implementation of the calculations for noble gases through reservoir modelling software with more sophisticated thermodynamic packages such as TOUGH (Jung et al. 2018) or MRST (Lie 2019) would allow to refine the performed calculations. The modelling could be adapted to the conditions of a specific storage site and processes like dissolution, mineralization and adsorption may be included to derive differential breakthrough curves for  $\text{CO}_2$  and noble gases. Thereby, the expected concentrations could be derived more precisely for various potential fluid migration pathways up to the surface and the estimates for the requirements on measurement and sampling technologies could be improved.

### 3. Conclusion and Outlook

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- **Capture Process:** The potential for further experimental studies is large. The continuous measurements and the single samples from the measurements at TCM and the other capture sites (Papers II and A.2) are inconclusive with regards to the influence of the capture process on the noble gas concentrations. The datasets and the approach with on-site mass spectrometry could be relevant for the characterization of engineering aspects of the absorption process. Different solubilities of different amines, absorber tower column setup, fluid withdrawal rate and degradation of the amine solvent were amongst the factors discussed to be most decisive over the resulting noble gas concentrations (Papers II and A.2).

Further studies may be conducted at TCM where a scientific campaign could be adapted to provoke differing parameters in the previously named process specifications. However, TCM is a large scale plant and it could be feasible to scale down the experiment to laboratory scale to reduce the free parameters and simplify boundary conditions, similar to the study by Buvik et al. 2021 which has so far mostly focused on O<sub>2</sub> solubility. Knowledge on noble gas solubilities could thereby be a very relevant constraint to relate the physical properties of the CO<sub>2</sub> during the absorption which are largely covered by the chemical reactions occurring. Thereby, capture process parameters may be optimized. In contrast, purely focusing on the implication for noble gases at storage site seems to be of minor priority since Papers II and III showed that the noble gas concentrations in the capture product are of minor importance to the likely signature during a leakage. An exception to this statement may be CO<sub>2</sub> captured from oxyfuel combustion processes which can result in enrichment of heavier noble gases, i.e. Kr and Xe, which may be retained during a leakage (Flude et al. 2017).

- **Leakage Quantification:** The possibilities of injection experiments are sheer endless: different fluid compositions, different tracers added, different patterns of tracers addition, different rock characteristics or different structural settings. These are all parameters one can change when performing experiments similar to Papers IV and B.1.

In my view, an important topic that should be addressed comes from the experience in one of the conducted field experiments: At the Svelvik CO<sub>2</sub> Field Lab (Sintef 2021) a part of the injected CO<sub>2</sub> was lost through the injection well (results not presented in this thesis). This experience was found to be the case during several other injection experiments (Roberts and Stalker 2017). Meanwhile, injection well leakage should be rather straight forward to detect, abandoned wells may be unmonitored, and quantification of such leakages would still be required. Considering that areas that are suitable for CO<sub>2</sub> storage are often in the vicinity of oil and gas production activity and especially attractive since parts of the necessary infrastructure are already installed. Such oil and gas activity typically comes with abandoned wells and for example in the whole North Sea there are tens of thousand abandoned wells (Böttner et al. 2020). Considering

that methane is released from those (Böttner et al. 2020), it is plausible that these could become conduits for CO<sub>2</sub> as well.

Not necessarily focusing on well leakages, experimental set-ups alike the offshore Stemm-CCS project at Goldeneye and others (Dean et al. 2020; Gros et al. 2021) could imitate a leakage and could make for fruitful applications of noble gases and portable mass spectrometers. Paper III discusses the application of the mobile mass spectrometer for leakage detection. They allow to sample suspected leakage sites, such as offshore fluid releases. Both water and gas analysis could be conducted on board of a ship to scan if elevated He concentrations indicate leaking CO<sub>2</sub> from a deep CO<sub>2</sub> source with a radiogenic signature. That similar objectives can be achieved, has been demonstrated in the vicinity of black smokers (Brennwald et al. 2016) or for methane leakages (Sommer et al. 2015). This could allow for direct leakage identification or an informed selection of samples for laboratory analysis and be an approach to introduce noble gases into standardized environmental surveys. Even installation of mass spectrometers on underwater vehicles and in-situ measurements may become available in the future.



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F., Cook, P., Guglielmi, Y., Nussbaum, C., Giardini, D., Mazzotti, M., and Wiemer, S. (2021). “Fault sealing and caprock integrity for CO<sub>2</sub> storage: an in situ injection experiment”. In: *Solid Earth* vol. 12, no. 2, pp. 319–343. DOI: 10.5194/se-12-319-2021.



# Papers





Paper I

# A Novel Approach To Quantify Air-Water Gas Exchange in Shallow Surface Waters Using High-Resolution Time Series of Dissolved Atmospheric Gases

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## Paper II

# Noble Gas Tracers in Gas Streams at Norwegian CO<sub>2</sub> Capture Plants

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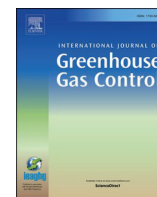






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journal homepage: [www.elsevier.com/locate/ijggc](http://www.elsevier.com/locate/ijggc)Noble gas tracers in gas streams at Norwegian CO<sub>2</sub> capture plantsUlrich W. Weber<sup>a,\*</sup>, Rolf Kipfer<sup>b,c</sup>, Edith Horstmann<sup>b</sup>, Philip Ringrose<sup>d,e</sup>, Niko Kampman<sup>f</sup>, Yama Tomonaga<sup>b</sup>, Matthias S. Brennwald<sup>b</sup>, Anja Sundal<sup>a</sup><sup>a</sup> Department of Geosciences, University of Oslo, 0371 Oslo, Norway<sup>b</sup> Eawag, Department of Water Resources and Drinking Water, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland<sup>c</sup> Institute for Geochemistry and Petrology, ETH Zurich, 8092 Zurich, Switzerland<sup>d</sup> Equinor ASA, 7005 Trondheim, Norway<sup>e</sup> Department of Geoscience and Petroleum, NTNU Trondheim, 7031 Trondheim, Norway<sup>f</sup> Shell Global Solutions International B.V., 1031 HW Amsterdam, Netherlands

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## ABSTRACT

Carbon capture and storage (CCS) may play a significant role in reducing greenhouse gas emissions. Noble gases are potential tracers to monitor subsurface CO<sub>2</sub> storage sites and verify their containment. Naturally occurring noble gases have been used successfully to refute alleged CO<sub>2</sub> leakage in the past.

We present results from several sampling campaigns at two Norwegian CO<sub>2</sub> capture facilities, the demonstration plant Technology Centre Mongstad (TCM) and the natural gas processing plant with CO<sub>2</sub> capture and storage on Melkøya. The gas streams in the capture plants were monitored with a combination of on-site mass spectrometry and subsequently analysed discrete samples. This allows us to define the factors controlling noble gas concentrations in captured CO<sub>2</sub>, to monitor temporal variation of noble gas concentrations and finally evaluate the potential to use noble gases as inherent environmental tracers for labelling CO<sub>2</sub> in storage reservoirs.

At both sites, CO<sub>2</sub> is captured using amine gas treatment. Noble gas concentrations in the gas streams were observed to decrease by several orders of magnitude during the processing. Isotopic ratios are air-like for CO<sub>2</sub> captured after natural gas combustion at TCM and natural gas-like for CO<sub>2</sub> captured from natural gas processing on Melkøya. Further, we detected a solubility trend caused by the amine solvent at TCM with higher solubility for heavier noble gases.

We find that the relative concentrations of noble gases in the captured CO<sub>2</sub> are defined by the gas from which the CO<sub>2</sub> is captured and the design of the amine gas treatment process. Both factors were observed to cause temporal variation in the captured CO<sub>2</sub>.

Using mixing and noble gas partitioning calculations we show that the significant depletion in noble gas concentrations, together with degassing of noble gas enriched formation water, means that the injected CO<sub>2</sub> will inherit the noble gas signature of the storage formation, even following the injection of significant CO<sub>2</sub> volumes. Any CO<sub>2</sub> leaked from the storage formation is thus likely to have a crustal noble gas signature, characteristic of the storage site, which can be targeted for monitoring.

## 1. Introduction

Rise of atmospheric CO<sub>2</sub> levels is causing significant climate change (IPCC, 2014) and nearly all countries have signed the Paris Agreement with the aim to keep global warming 'well below 2 °C' (United Nations, 2015). Carbon capture and storage (CCS) may become an important climate change mitigation technology needed to achieve the 2 °C goal (IPCC, 2014; Metz et al., 2005; van Vuuren et al., 2011; Rogelj et al.,

2018).

Large scale application of CCS requires compliance with environmental regulations and to support public acceptance sophisticated monitoring has to be in place (IEAGHG, 2015; Khashgi et al., 2012). Even though, leakage likelihood of storage sites is estimated to be very low (Alcalde et al., 2018).

There is a manifold of geophysical (e.g. time lapse seismics) and geochemical (e.g. pH) monitoring tools available to detect CO<sub>2</sub> and

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verify containment in geological storage formations (IEAGHG, 2015). Commonly used set ups are, however, not necessarily sufficient to differentiate the gas origin of an observed anomaly. Evaluation of the noble gas signatures, concentrations and isotopic ratios in injected, anthropogenic CO<sub>2</sub> can allow differentiation from natural, geological and biologically produced, CO<sub>2</sub> (Holland and Gilfillan, 2012; Flude et al., 2016; Mackintosh and Ballentine, 2012; Shelton et al., 2016; Györe et al., 2015). This was demonstrated successfully at an alleged leakage case at the Weyburn-Midale CO<sub>2</sub> injection project (Gilfillan et al., 2017). Further, noble gases are chemically inert, hence, in contrast to CO<sub>2</sub> and other tracers, environmentally safe and not subject to chemical and biological processes (Holland and Gilfillan, 2012). Noble gases are widely applied as environmental tracers: inherent and naturally occurring in all terrestrial fluids (Burnard, 2013), and may therefore be a very cost-effective monitoring tracer (Roberts et al., 2017).

A baseline dataset for inherent, naturally occurring (not artificially added), noble gases in captured CO<sub>2</sub> from several sites was established in Flude et al., 2017. Generally, noble gas concentrations were found to decrease during the CO<sub>2</sub> absorption process at several capture plants. In the ICO<sub>2</sub>P project (ICO<sub>2</sub>P, 2020), we focus on establishing such a dataset for the CCS projects in Norway (Fig. 1). Further, we aim to contribute to the full-scale CCS project initiated by the Norwegian state and industry that combines onshore capture operations such as a cement plant with offshore storage in the North Sea (Fig. 1), aimed to be operating in 2024 (CCS Project, 2020; Norwegian Petroleum Directorate, 2016; Global CCS Institute, 2018).

From previous studies, it is not evident that noble gases in a single sample from CO<sub>2</sub> capture streams are representative of the overall noble gas signature, due to potential temporal variation. Therefore, we apply a novel sampling strategy in this study, monitoring gas streams on-site using a mobile mass spectrometer (Brennwald et al., 2016), combining time series of in-line sampling, with discrete gas sample analysis using a

lab-based mass spectrometer with higher analytical precision.

We observe temporal variation in the CO<sub>2</sub>-rich fluxes and aim to determine the parameters controlling noble gas concentrations and the inherent variation. Finally, we discuss the implications of our sampling approach on monitoring CO<sub>2</sub> injection streams and put the identified noble gas signatures into perspective for future usage in leakage detection or in verification of storage containment.

## 2. Material and methods

### 2.1. CO<sub>2</sub> capture – amine gas treatment

Amine gas treatment is currently the most mature CO<sub>2</sub> capture technology (Rochelle, 2009; Leung et al., 2014) and is used at both study sites. In this process, CO<sub>2</sub> in the incoming flue gas, e.g. the exhaust from a power plant, reacts with an aqueous amine solvent in the absorber (e.g. (Rao and Rubin, 2002); Fig. 2). The CO<sub>2</sub>-rich amine solution is transferred to the stripper where it is heated, releasing the CO<sub>2</sub> as gas with a concentration of up to 99% in the final gas mixture (Rao and Rubin, 2002; Dutcher et al., 2015). The heat required in the regeneration step poses an energy and cost penalty for a capture plant. The CO<sub>2</sub> depleted amine solvent is brought back to the absorber to close the cycle. With amine absorption a capture efficiency of 75–90% of the CO<sub>2</sub> in the flue gas is achieved (Rao and Rubin, 2002).

In the following, the sampling point before the absorber is referred to as ‘Input’. The sampling point after the stripper is referred to as ‘Output’ (Fig. 2).

Noble gases do not react with the aqueous amine solvent, but physically dissolve to reach equilibrium between the dissolved and the gas phase. Phase partitioning at equilibrium can be described by Henry’s law, which in its simplest form states that the dissolved concentration depends on the partial pressure of a gas species and its specific,

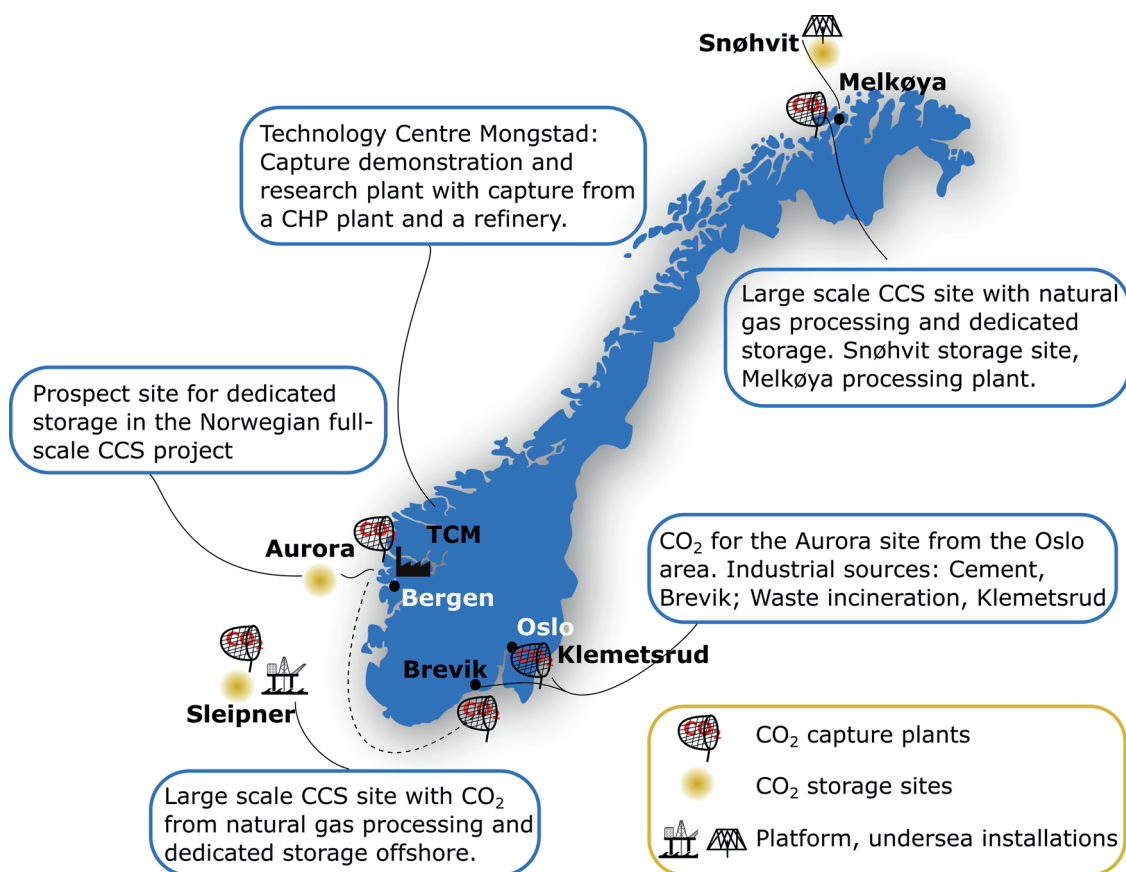


Fig. 1. CCS in Norway. For this study, sampling was conducted onshore at the Technology Centre Mongstad (TCM) and at Melkøya.

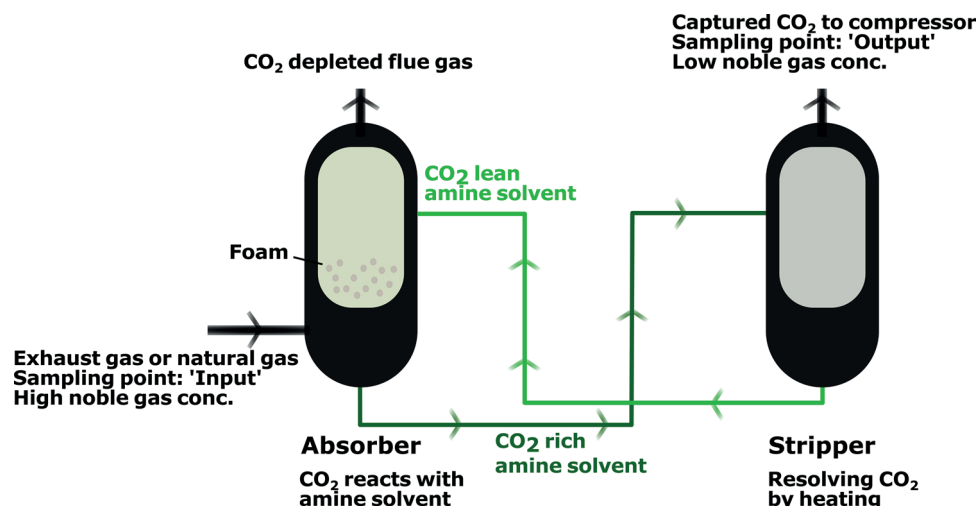


Fig. 2. Sketch of the amine capture process with the ‘Input’ and ‘Output’ sampling points labelled. CO<sub>2</sub> is captured by amine gas treatment in the absorber and released again in the stripper. After the process, the captured CO<sub>2</sub> will be compressed for transport.

temperature-dependent solubility for the respective solvent (Henry’s constant).

Foam can develop in the absorber due to gas bubbles stabilizing on surfactants or contaminants in the amine solvent (Thitakamol and Veawab, 2008). Bubble-mediated physical gas exchange might then introduce additional gases into the amine solution. A foam-inhibitor chemical can be added to prevent foam formation.

## 2.2. Study sites

### 2.2.1. Melkøya

Melkøya (Equinor, 2020a), with its respective storage site Snøhvit, is after Sleipner (Equinor, 2020b) (Fig. 1), the second Norwegian commercial large-scale CCS site. It is located close to Hammerfest and was established in 2007 (Hansen et al., 2013).

The natural gas from the Snøhvit Field naturally contains 5–8% CO<sub>2</sub>. The CO<sub>2</sub> is removed from the natural gas onshore at Melkøya before the gas is combusted. A solvent based on activated Methyldiethanolamine (aMDEA) is used for the amine gas treatment process. The facility runs with an approximate capture capacity of 0.7 MtCO<sub>2</sub>/a (Hansen et al., 2013), and 6.48 Mt have been injected by the end of 2019. In comparison, annual CO<sub>2</sub> emissions from the Norwegian oil and gas sector are approximately 15 Mt (Statistics Norway, 2019). The natural gas is then shipped to energy markets as liquified natural gas (LNG), meanwhile the captured CO<sub>2</sub> is injected into the Stø Formation at >2000 m depth in the vicinity of the Snøhvit Field (Halland et al., 2013).

### 2.2.2. Technology Centre Mongstad

The CO<sub>2</sub> capture demonstration plant Technology Centre Mongstad (TCM) (TCM DA, 2020) is located north of Bergen (Fig. 1) and is one of the world’s largest research facilities for non-proprietary testing of CO<sub>2</sub> absorption using amine gas treatment, mainly using monoethanolamine (MEA) as solvent (Faramarzi et al., 2017; Morken et al., 2017).

CO<sub>2</sub> is captured either from (i) the exhaust stream of a combined heat and power plant (CHP), which combusts natural gas and refinery fuel gas (RFG) from the nearby Mongstad refinery, or (ii) the residue fluid catalytic cracking (RFCC) flue gas of the Mongstad refinery processing oil and gas from the North Sea.

Combustion at the CHP plant introduces air into the gas stream and this part of the CO<sub>2</sub> captured at TCM is an example for a post-combustion capture plant (Leung et al., 2014). For CHP flue gas, the CO<sub>2</sub> content is at 3.5–4%. In the case of RFCC flue gas, the gas is not combusted before capture but air is mixed in to keep the CO<sub>2</sub> concentration at constant levels during capture tests (Shah et al., 2018). CO<sub>2</sub> concentrations are

12–15% and this flue gas source is considered equivalent to flue gas from coal power plants (Shah et al., 2018).

TCM has a total capturing capacity of 0.1 MtCO<sub>2</sub>/a (TCM DA, 2020). During an expansion of the Norwegian CCS project, an inclusion of CO<sub>2</sub> captured at TCM could be a valid proposition.

## 2.3. Methods

### 2.3.1. Noble gas analysis in discrete gas samples

Discrete samples were collected in stainless steel cylinders (Swagelok, volume: 40 cm<sup>3</sup>) complementary to the continuous measurements. The cylinders were connected to the sampling lines, flushed for several minutes to avoid air contamination and closed with stainless steel needle valves.

The discrete samples were analysed at the noble gas laboratory at ETH Zurich, Switzerland (Beyerle et al., 2000). Here, noble gas analysis by static mass spectrometry reaches a typical overall error of ±1% for concentrations, ≤1% for isotopic ratios and has low detection limits due to gas purification steps (Beyerle et al., 2000).

A set of gas samples were sampled on 31.08.2018 at Melkøya. At TCM, several samples were collected accompanying the continuous measurements.

### 2.3.2. Continuous noble gas analysis

Noble gas partial pressures were measured continuously on-site at the Input and Output sampling points at TCM using the portable mass spectrometer ‘miniRuedi’ (Gasometrix GmbH, Switzerland; Fig. 3 top). Technical details of the mass spectrometer can be found in Brennwald et al. (2016). It was formerly mainly used in aquatic science but also applied for the monitoring of trial runs for radioactive waste disposal (Weber et al., 2019; Tomonaga et al., 2019).

The instrument measures ion currents on selected m/z-ratios with a Faraday detector and an electron multiplier. Partial pressures are derived from peak-height comparison with a calibration gas.

Typically, the m/z-ratios for N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> were measured on the Faraday detector, <sup>40</sup>Ar on Faraday detector and multiplier and <sup>4</sup>He, CH<sub>4</sub> and <sup>84</sup>Kr on the multiplier. With that set-up, a sampling point was measured approximately every 15 minutes and a calibration was conducted approximately every hour. From 02.10.-05.10.2018 only CO<sub>2</sub>, CH<sub>4</sub>, <sup>40</sup>Ar and <sup>4</sup>He were measured to increase sampling frequency to approximately 10 min.

During the first measurement period, 11.07.-25.07.2018, air was used as calibration gas. A tailored calibration gas mixture (made on order by Praxair Inc.) was prepared for the second measurement period,

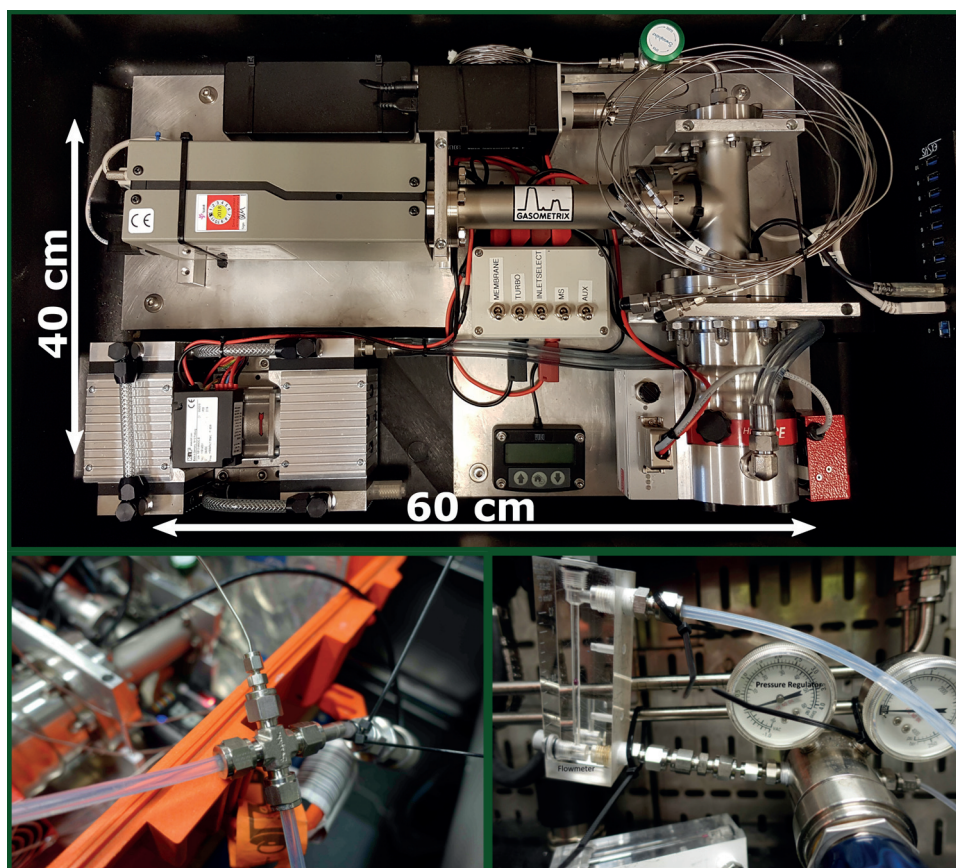


Fig. 3. Top: The portable mass spectrometer 'miniRuedi'. Bottom, left: Inlet to the mass spectrometer (cross connection): Flow-by gas stream and inlet to mass spectrometer and monitoring pressure sensor. Bottom, right: Setup before the inlet to the mass spectrometer: Flow-meter (left) and pressure regulator (right).

25.09.-05.10.2018. It consisted of 10 ppm of each noble gas (He, Ne, Ar, Kr, Xe), 1% CH<sub>4</sub> and 99% CO<sub>2</sub> to mimic the high CO<sub>2</sub> content of the captured CO<sub>2</sub>. The calibration gases were filled into a Plastigas®-bag during the experiments. Basic stainless steel connections were used for the attachment to the sampling points (Fig. 3, bottom left). Pressure regulators were installed before the inlet to the mass spectrometer in order to sample the gas at the same pressure as the standard gas, i.e. atmospheric pressure (Fig. 3, bottom right).

In 2017, we conducted a feasibility study at TCM to investigate the applicability of a portable mass spectrometer on site for continuous analysis (Sundal et al., 2018). Two additional time series were subsequently collected in summer and fall 2018, specifically from 11.07.-25.07.2018 and 25.09.-05.10.2018.

### 3. Results

#### 3.1. Discrete samples

The noble gas concentrations and isotopic ratios of the discrete samples (In- and Output (see Fig. 1)) both from TCM and Melkøya are shown in Table 1. Isotopic ratios are given in Table 2. The results from Melkøya provide, to our knowledge, the first dataset for noble gases of a large scale natural gas processing site.

#### 3.2. Continuous noble gas time series

##### 3.2.1. Helium

The first time series (11.07.-25.07.2018) recorded with the on-site mass spectrometer at TCM shows He concentrations to vary considerably at the Input ( $\pm 30\%$ ) (Fig. 4[a]). Due to low concentrations, detection limit  $\approx 0.45$  ppm, it was not possible to measure the He at the

Output sampling point with on-site mass spectrometry.

The variation appears to be linked to the percentage of refinery fuel gas (RFG) added to natural gas combustion at the CHP plant (Fig. 4[b]). The RFG share was typically slightly above 50%, but shares as low as 20% were also applied. With high content of RFG, the He concentration is low and vice versa. The two time series correlate with  $\rho \approx 0.8$  (Pearson correlation coefficient).

During the second monitoring period (25.09.-05.10.2018), first a CHP-derived flue gas and then only residue fluid catalytic cracking (RFCC) flue gas was analysed (see Fig. 5). The change of input gas is again observed in He concentrations which are lowered by  $\approx 40\%$  (Fig. 5).

The capture plant had to be shut down for a two day period in order to change the set-up to run in high CO<sub>2</sub> inlet concentration mode; from  $\approx 4\%$  to  $\approx 12\%$ . Technical changes in the plant were conducted in a second, shorter period. This caused the CO<sub>2</sub> stream to be interrupted and air-contaminated, which was also observed by low CO<sub>2</sub> partial pressures measured by the miniRuedi. Those periods are not shown in Fig. 5. Measurements of discrete samples agree with the in-line measurements and are depicted in Fig. 5.

##### 3.2.2. Argon

In the captured CO<sub>2</sub> stream at TCM, only Ar was detectable with continuous measurements. Simultaneous calibration of Input and Output did not succeed since only air was available as calibration gas during this monitoring period (11.07.-25.07.2018). In air, Ar was measured on the Faraday detector and in saturation on the multiplier, meanwhile the Output had to be measured on the multiplier due to its significantly lower concentrations after absorption. Therefore, the Output values on  $m/z = 40$  are depicted in the ion current, given in ampere, measured with the multiplier detector. The current has then



**Table 1**  
Noble gas concentrations given in  $\text{cm}^3_{\text{STP}}/\text{cm}^3_{\text{STP}}$ , with  $p_{\text{STP}}=1 \text{ atm}$  and  $T_{\text{STP}}=0^\circ \text{C}$  (total concentrations, if not other stated). Atmospheric values from Sano et al. (2012). Uncertainties are one standard deviation.

#	Sample point	Source	Sample date	He	Ne	Ar	Kr	Xe	Lab Name
		Atmosphere		5.24E-06	1.82E-05	9.34E-03 <sup>36</sup> Ar: 3.13E-05	1.14E-06	9.0E-08	
<i>Technology Centre Mongstad (TCM)</i>									
1	Input	CHP	12.07.2018	9.15E-06 ± 7.55E-08	1.88E-05 ± 9.38E-08	<sup>36</sup> Ar: 2.90E-05 ± 4.51E-08	1.17E-06 ± 5.83E-09	8.13E-08 ± 1.36E-09	TCM 2005
2	Output	CHP	12.07.2018	3.27E-09 ± 1.77E-10	4.37E-09 ± 1.96E-10	3.66E-06 ± 2.13E-08	7.32E-10 ± 1.59E-11	1.22E-10 ± 1.06E-11	TCM 2001
3	Input	CHP	25.07.2018	8.36E-06 ± 6.91E-08	1.82E-05 ± 9.14E-08	<sup>36</sup> Ar: 2.82E-05 ± 3.48E-08	1.14E-06 ± 5.02E-09	8.82E-08 ± 1.41E-09	TCM 2006
4	Input	CHP	26.09.2018	9.68E-06 ± 7.99E-08	2.05E-05 ± 1.03E-07	1.03E-02 ± 4.71E-05	1.24E-06 ± 8.28E-09	9.43E-09 ± 4.32E-10	TCM 2011
5	Input	RFCC	02.10.2018	5.57E-06 ± 4.60E-08	1.96E-05 ± 9.78E-08	9.96E-03 ± 4.56E-05	1.22E-06 ± 5.69E-09	8.93E-08 ± 1.59E-09	TCM 2013
6	Output	RFCC	02.10.2018	1.68E-09 ± 5.08E-10	4.30E-09 ± 2.67E-10	4.78E-06 ± 3.02E-08	1.00E-09 ± 2.22E-11	1.84E-10 ± 1.68E-11	TCM 2014
7	Input	RFCC	05.10.2018	5.55E-06 ± 4.58E-08	1.92E-05 ± 9.63E-08	1.65E-03 ± 1.17E-05	1.98E-07 ± 9.21E-10	1.55E-08 ± 2.66E-10	TCM 2016
<i>Melkøya: Natural gas processing</i>									
8	Untreated gas	Nat. gas	31.08.2018	1.22E-04 ± 1.01E-06	6.39E-08 ± 5.23E-09	5.66E-05 ± 3.14E-07	9.43E-09 ± 4.32E-10	2.00E-09 ± 1.89E-10	HAMM 2007
9	Input	Nat. gas	31.08.2018	1.29E-04 ± 1.06E-06	5.73E-09 ± 1.16E-09	1.75E-05 ± 8.62E-08	1.57E-09 ± 8.85E-11	5.26E-10 ± 5.86E-11	HAMM 2008
10	Output	Nat. gas	31.08.2018	2.86E-06 ± 2.36E-08	1.75E-09 ± 3.05E-10	1.01E-06 ± 1.05E-08	5.29E-11 ± 1.19E-11	3.73E-11 ± 7.52E-11	HAMM 2009
11	During compr.	Nat. gas	31.08.2018	2.64E-06 ± 2.18E-08	1.01E-08 ± 5.55E-10	3.23E-06 ± 3.69E-08	6.36E-11 ± 1.31E-11	3.96E-11 ± 2.33E-11	HAMM 2010

**Table 2**

Isotopic ratios for the samples as described in Table 1. Atmospheric values from (Sano et al., 2012). The  $^3\text{He}/^4\text{He}$ -ratios are also reported in the Ra-notation where Ra is the  $^3\text{He}/^4\text{He}$ -ratio of atmospheric air (i.e.  $1.39\text{E}-06$ ; see e.g. Sano et al., 2012). Uncertainties are one standard deviation. Undetectable ratios with the system described in Beyerle et al. (2000) are noted with n.d., those not measured with –.

#	$^3\text{He}/^4\text{He}$	$^3\text{He}/^4\text{He}$ ([Ra])	$^{22}\text{Ne}/^{20}\text{Ne}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{86}\text{Kr}/^{84}\text{Kr}$	$^{136}\text{Xe}/^{129}\text{Xe}$	$^{136}\text{Xe}/^{134}\text{Xe}$
<b>Atmosphere</b>	1.34E-06	1.000	0.1022	296	0.303	0.335	0.849
<i>Technology Centre Mongstad (TCM)</i>							
1	$8.55\text{E}-07 \pm 5.15\text{E}-09$	$0.638 \pm 0.006$	$0.1023 \pm 0.0001$	–	$0.306 \pm 0.001$	$0.345 \pm 0.004$	$0.888 \pm 0.012$
2	$9.35\text{E}-07 \pm 1.24\text{E}-07$	$0.698 \pm 0.092$	$0.0701 \pm 0.0241$	$364 \pm 73$	$0.312 \pm 0.006$	$0.358 \pm 0.015$	$0.922 \pm 0.052$
3	$9.20\text{E}-07 \pm 7.98\text{E}-09$	$0.687 \pm 0.006$	$0.1021 \pm 0.0001$	–	$0.306 \pm 0.001$	$0.343 \pm 0.003$	$0.878 \pm 0.005$
4	$9.28\text{E}-07 \pm 5.72\text{E}-09$	$0.692 \pm 0.004$	$0.1020 \pm 0.0001$	$320 \pm 24$	$0.304 \pm 0.001$	$0.326 \pm 0.002$	$0.864 \pm 0.013$
5	$1.23\text{E}-06 \pm 1.27\text{E}-08$	$0.919 \pm 0.010$	$0.1020 \pm 0.0001$	$321 \pm 24$	$0.307 \pm 0.001$	$0.323 \pm 0.002$	$0.832 \pm 0.007$
6	$2.37\text{E}-06 \pm 2.35\text{E}-07$	$1.765 \pm 0.175$	$0.2459 \pm 0.0298$	$371 \pm 51$	$0.303 \pm 0.006$	$0.318 \pm 0.009$	$0.875 \pm 0.039$
7	$1.34\text{E}-06 \pm 8.80\text{E}-09$	$1.002 \pm 0.007$	$0.1020 \pm 0.0001$	$324 \pm 24$	$0.306 \pm 0.001$	$0.338 \pm 0.003$	$0.871 \pm 0.009$
<i>Melkøya: Natural gas processing</i>							
8	$2.45\text{E}-08 \pm 1.01\text{E}-09$	$0.018 \pm 0.001$	$0.1125 \pm 0.0368$	$636 \pm 244$	$0.303 \pm 0.011$	$0.319 \pm 0.009$	$0.719 \pm 0.039$
9	$2.51\text{E}-08 \pm 1.22\text{E}-09$	$0.019 \pm 0.001$	$0.3667 \pm 0.0952$	n.d.	$0.313 \pm 0.015$	$0.303 \pm 0.016$	$0.712 \pm 0.043$
10	$2.84\text{E}-08 \pm 1.58\text{E}-09$	$0.021 \pm 0.001$	$0.1823 \pm 0.0727$	n.d.	$0.224 \pm 0.013$	$0.338 \pm 0.020$	$0.834 \pm 0.035$
11	$2.64\text{E}-08 \pm 1.58\text{E}-09$	$0.020 \pm 0.001$	$0.0669 \pm 0.0942$	n.d.	$0.270 \pm 0.011$	$0.293 \pm 0.019$	$0.786 \pm 0.062$

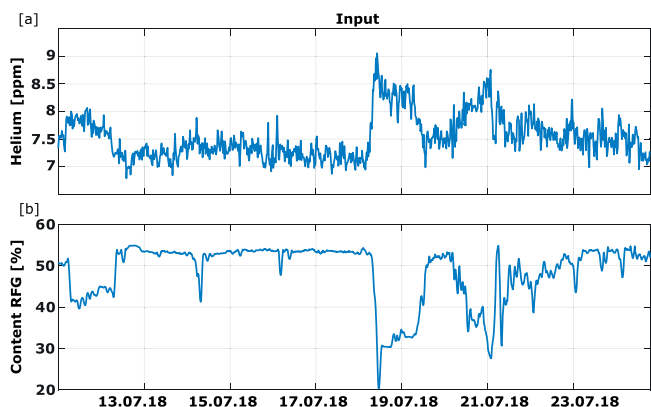


Fig. 4. [a] Time series of He concentration of the Input at TCM from 11.07.-25.07.2018 in [ppm]. Typical measurement precision: 2.5%. [b] Time series of relative content of RFG in the gas mixture combusted at the CHP plant in [%]. A strong negative correlation between the concentration and the relative share of RFG gas is observed.

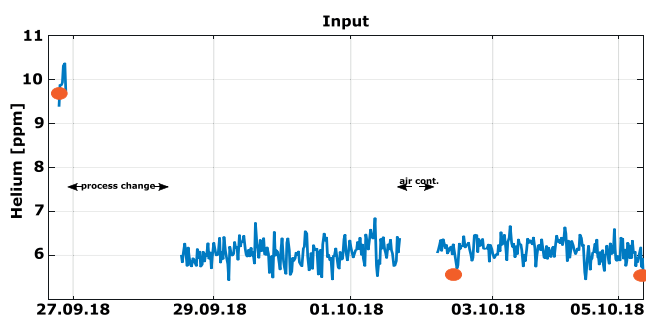


Fig. 5. Time series of He concentration of the Input at TCM from 26.09.-05.10.2018 in [ppm]. Typical measurement error: 3%. Two periods where the plant did undergo technical changes. First period is when the switch from CHP's exhaust to only RFCC gas was conducted. Orange dots are the data from the discrete samples (Table 1).

been corrected with the standard measurements on  $m/z = 4$ , since this mass-charge ratio is also measured on the multiplier.

Even though the values are not calibrated, the observations made are worth mentioning. During the time period, Input Ar intensities do not show significant variation (Fig. 6[a]). These Ar concentration can be used to infer the missing  $^{40}\text{Ar}$  values in Table 1. In contrast to the Input, there

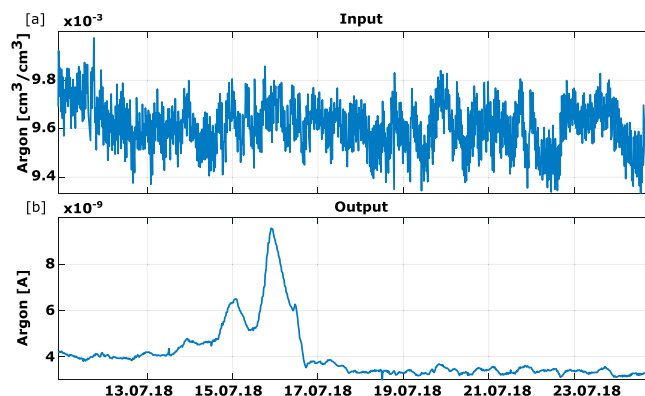


Fig. 6. Time series of Ar [a] of the Input [ $\text{cm}^3/\text{cm}^3$ ] and [b] the Output on  $m/z = 40$  in ampere [A] at TCM during 11.07.-25.07.2018. Typical measurement precision: 2.5%. Temporal variation in the Output seems unrelated to the Input.

is an increase in Output Ar intensities (Fig. 6[b]). The temporal variation during 15.07.2018 and 16.07.2018 in the Output gas shows no relation to the Ar concentration of the Input. Further, none of the parameters monitored in the plant such as pressure, solvent temperature or gas release temperature in the stripper correlate to the temporal variation of Ar.

## 4. Discussion

### 4.1. Effect of the flue gas

A significant control on the noble gas concentrations in the captured  $\text{CO}_2$  is the source of the flue gas, synonymous to the Input sampling point in this study, from which  $\text{CO}_2$  is captured. The samples from the post-combustion and RFCC (TCM) and the natural gas processing (Melkøya) plant show significantly different noble gas concentrations both at the Input (Fig. 7[a]) and at the Output sampling points (Fig. 7 [b]).

In the Input to the absorber at Melkøya, concentrations differ strongly from atmospheric values, i.e. He is enriched whereas the other noble gases are strongly depleted (Fig. 7[a]). This is common for natural gas which is enriched in radiogenic  $^4\text{He}$  from the reservoir rock (Prinzhofer, 2013). Isotopic ratios representing the natural gas source, note the low  $^3\text{He}/^4\text{He}$ , are mostly conserved during gas processing and  $\text{CO}_2$  absorption (Table 2). Captured  $\text{CO}_2$  from Melkøya contains significantly higher He concentrations than previously observed at other

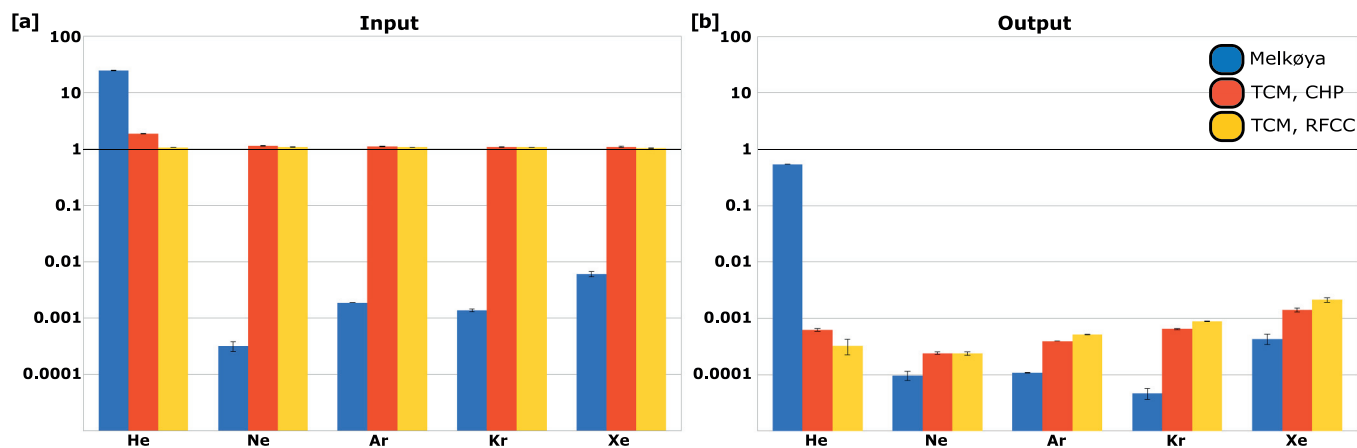


Fig. 7. Observed noble gas concentrations relative to their atmospheric concentrations showing almost atmospheric values for TCM Input samples #4 CHP and #5 RFCC and a natural gas signature for Melkøya, sample #9. After the capture process noble gas concentrations are orders of magnitude lower than in air. Output samples #2 CHP, #9 RFCC for TCM and #14 for Melkøya (Table 1). Uncertainties one standard deviation.

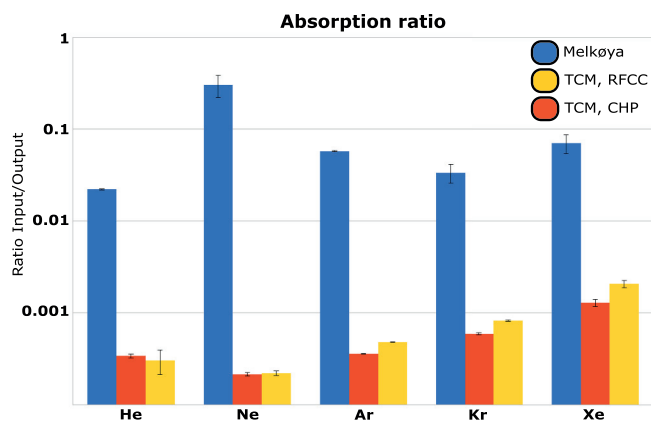


Fig. 8. Absorption ratios TCM and Melkøya. Calculated from the samples in Fig. 7. Uncertainties one standard deviation.

capture facilities (Gilfillan et al., 2017; Flude et al., 2017).

In the Input at TCM, noble gas concentrations are at or near atmospheric levels as depicted in Fig. 7[a]. This is a clear indication that combustion has introduced atmospheric noble gases, since air is used as oxygen supply for the CHP flue gas. The signature of the RFCC flue gas is derived from the air mixed in to stabilize CO<sub>2</sub> concentrations. He contents are high in source gas, and can still be significantly enriched relative to atmospheric equilibrium before capture, indicating the fossil origin (He enrichment) of the natural gas prior to combustion. The changing He content leads to slightly varying <sup>3</sup>He/<sup>4</sup>He ratios at different dates. Flue gas from post-combustion sources, including waste incineration or bio-energy combustion, will have a signature close to air, especially when a radiogenic component from fossil fuels is not present.

Table 3

Henry's law constants ratio for water relative to Xe at 298.15 K from (Sander, 1999) and measured values from samples #5 and #6 at TCM with RFCC as source (Table 1). Uncertainties are one standard deviation.

gas species i	He	Ne	Ar	Kr	Xe
$k_{H,Xe}/k_{H,i,water}$	11.3	9.56	3.07	1.79	1
at TCM	6.8 ± 2.2	9.4 ± 1.2	4.3 ± 0.4	2.5 ± 0.3	1

#### 4.2. Temporal variation in flue gas

The results from TCM show that the flue gas stream from which the CO<sub>2</sub> is captured can have temporal variation in noble gas concentrations. He concentrations at In- and Output correlate to the gas mixture that is combusted and subsequently fed to the absorber (Figs. 4 and 5).

The analysed discrete samples collected from the Output confirm that the variation in the Input shown in Fig. 5 is also present after the absorption process; i.e. Output samples #2 and #6 (Table 1) show a decrease of 50 ± 15 % in the He concentrations. Concentrations for Kr (increase of ≈40 ± 5 %) and Xe of the two samples also change in the Output (increase of ≈50 ± 20 %).

#### 4.3. Effect of the absorption process

A comparison between different absorption processes of carbon capture plants is difficult since many parameters of the process design, e.g. the absorber column and stripper internals, the liquid withdrawal configuration and the operating pressure regimes, are specific to each site. Their influences on the solubility and absorption of noble gases are briefly discussed below. A quantification of the impact of single parameters on the noble gas concentration in captured CO<sub>2</sub> is, however, beyond the scope of this study.

##### 4.3.1. Absorption ratios

The data reflect that there are significant differences in the capture process at the two study sites. Absorption ratios of noble gases in the amine solvent are determined by dividing Output by Input concentrations (Fig. 8).

At Melkøya, noble gases are absorbed more efficiently, by two orders of magnitude, than at TCM, since the absorption ratio is higher. The remarkably different absorption ratios could be caused by the differences in the operating pressure, i.e. approximately 66 bar at Melkøya and 1.02 bar at TCM, and overall plant design. Further, CO<sub>2</sub> mass transfer was shown to be proportional with solvent temperature and circulation rates, which could also hold true for noble gases (Dey and Aroonwilas, 2009), and provide a site specific imprint on the chemical and isotopic signature.

It has been shown for N<sub>2</sub>O that solubility is varying systematically in a suit of amine solvents in Penttilä et al., 2011. This will also hold true for noble gases in this case (MEA at TCM and aMDEA at Melkøya). Further, the addition of foam-inhibitor chemical might affect the solubility of gases in the solvent by reducing surface tension (Uhlig, 1937).

Foam development and subsequent gas entrainment is a severe

operational problem in the capture process (Thitakamol and Veawab, 2008) and may add quantitatively to the physical absorption process. Foam development was reported by the local operators to occur at Melkøya, causing introduction of CH<sub>4</sub> from the natural gas during foaming into the produced CO<sub>2</sub> without having received more detailed information. Consequently, noble gases would also be introduced increasingly in this way, explaining the observed differential absorption ratios at Melkøya.

#### 4.3.2. Solubility trend

At TCM, the absorption ratios show a clear solubility trend towards heavier noble gases, i.e. for Xe the absorption ratio is about one order of magnitude higher than for e.g. Ne and, hence, relatively more Xe is found in the captured CO<sub>2</sub> stream (Fig. 8). The trend roughly follows the Henry's law constants ratios for water  $k_{H,Xe}/k_{H,i}$ , since the solvents are aqueous solutions, e.g. 30 wt% MEA in water, (Table 3; Henry's law constants at 298.15 K; values from Sander (1999)). For TCM, a simple form of Henry's law seems to describe the capture process reasonably well.

Henry coefficients for noble gases in water seem to be a valid approximation for the relative solubility of noble gases. However, absolute Henry's law solubility constants for noble gases vary significantly from water. Determining the absolute solubilities based on our measurements or from literature could only be a rough estimation since it is not ensured that full equilibrium is reached and because the composition of the solvent is not properly known, due to proprietary reasons. An ideal mixing rule for solubilities in such aqueous solutions has been shown to be hardly applicable for N<sub>2</sub>O (Kierzkowska-Pawlak and Zarzycki, 2002). The 'N<sub>2</sub>O analogy' for modelling the capture process of CO<sub>2</sub> lacks empirical basis to be universally applied (Monteiro and Svendsen, 2015; Kierzkowska-Pawlak and Zarzycki, 2002). Results from more systematic and controlled studies of noble gas solubilities in amine solvents could constrain Henry's law better.

#### 4.3.3. Temporal variation in absorption process

Ar concentrations were observed to vary significantly in response to operational changes in the capture process during a feasibility study conducted at TCM in 2017 (Sundal et al., 2018). Captured CO<sub>2</sub> was recycled into the absorber, to simulate higher CO<sub>2</sub> contents in the flue gas. A decrease of the recycling ratio during the feasibility study was found to correlate with a decrease in relative Ar content.

Temporal variation at the Output, which cannot be associated with deliberate and known processes and/or source changes at the plant (e.g. during the measurement period shown in Fig. 6), is likely to be caused by slight changes in process parameters such as foam-inhibitor injection and its frequency, addition of surfactants, temperature or pressure fluctuations. It is very probable that temporal variation in noble gas composition is caused by the amine absorption process, although this could not be quantified with the current set-up and available dataset.

### 4.4. Implications on monitoring

#### 4.4.1. Monitoring of noble gas signatures in captured CO<sub>2</sub>

Our findings show that a single sample may not be representative for the noble gas signature of captured CO<sub>2</sub> from a given capture plant. The data suggest that injected CO<sub>2</sub> derived from several capture plants, such as the full-scale CCS project in Norway, may span several orders of magnitude for a single noble gases' concentration. A monitoring routine, such as presented herein, should therefore be in place before the injection, documenting the final CO<sub>2</sub> product where the gas streams from several plants are mixed. In the specific case of mixing captured CO<sub>2</sub> from a waste incineration plant and a cement plant, as proposed in the Norwegian full-scale CCS project, we expect noble gas signatures to be air-like, similar to those from other post-combustion sources (e.g. TCM), as air is used for combustion. Monitoring of the gas streams may be of minor priority at these plants.

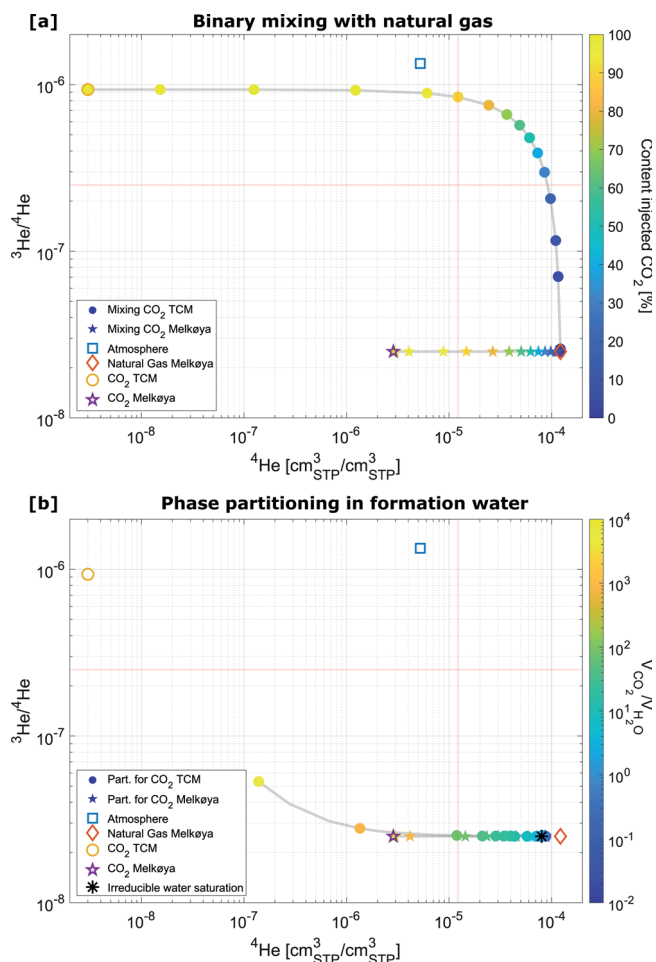


Fig. 9. [a] Mixing of <sup>4</sup>He and <sup>3</sup>He/<sup>4</sup>He in captured CO<sub>2</sub> at Melkøya, sample #11, and TCM, sample #2 with natural gas at Melkøya, sample #8 (samples in Table 1) as function of the CO<sub>2</sub> content in the mixture. [b] Calculated noble gas signature for the same samples after equilibration with formation water in dependence of the V<sub>CO<sub>2</sub></sub>/V<sub>H<sub>2</sub>O</sub>-ratio. The irreducible water saturation ratio, V<sub>CO<sub>2</sub></sub>/V<sub>H<sub>2</sub>O</sub> ≈ 1.5, marks the value at the mean maximum observed CO<sub>2</sub> saturation in reservoir rocks (Burnside and Naylor, 2014). Exemplary, values are derived for depth and temperature conditions approximately found at the Snøhvit storage site: Depth of 2250 m, temperature 84.8 °C. Red lines mark one order of magnitude perturbation from natural gas at Melkøya.

Baseline datasets, such as the relation of noble gas concentration to the gas mixture combusted at a CHP plant (see Fig. 4[b]), can then be used to parameterize the noble gas concentrations in the captured CO<sub>2</sub> once the signatures in the contributing gas streams are known. In this way, sampling frequency could be reduced and a representative estimate becomes available without extensive sampling, at low cost.

For natural gas processing plants such as at Melkøya, temporal variation may also be observed when natural gas streams from several reservoirs/wells are mixed and processed. Different geological settings (i.e. burial depths, migration paths, hydrocarbon sources) can lead to varying degrees accumulation and overall isotopic signatures. Significant variation in the He content of fossil hydrocarbon resources were e.g. observed in different wells within the Magnus Field in the North Sea (Ballentine et al., 1996). A correlation between producing wells could then be used to estimate the resulting noble gas signatures, once they are mixed with each other and have gone through the capture process.

#### 4.4.2. Storage site monitoring

In this chapter, we discuss the implications of the observed noble gas signatures at capture plants for their applicability as monitoring tracers.

As described, noble gas concentrations in the captured, and subsequently injected, CO<sub>2</sub> are typically low due to the CO<sub>2</sub> absorption process. The absorption process can also imprint a site specific signature on the injected CO<sub>2</sub>. While isotopic ratios of one noble gas are not significantly altered in our samples (see Table 2), absolute concentration ratios can change significantly during absorption (see Fig. 8 and Section 4.3.2). Thus, noble gas content can potentially differentiate injected gas from natural background fluids such as fossil gas (CH<sub>4</sub> and CO<sub>2</sub>), biogenic CO<sub>2</sub>, formation water or an atmospheric signature, either due to differences in isotopic ratio, elemental ratio or by absolute concentrations.

Leakage scenarios can be evaluated using binary (or ternary) mixing analysis between fluid components and the known elemental and isotopic composition of the background fluid(s). The threshold for leakage detection can be quantified and is reached at a significant perturbation from the background noble gas signature. We considered a minimum perturbation of one order of magnitude to be necessary for the discrimination of injected CO<sub>2</sub> and native fluids, accounting for detection or sampling uncertainties and variability in the background values. There is prior evidence that such perturbations are suitable for detection of different fluid sources, e.g. at the large scale CO<sub>2</sub>-EOR (Enhanced Oil Recovery) site Cranfield (Györe et al., 2015). At the Kerr site, mixing analysis using He-signatures was used to exclude a major contribution of injected CO<sub>2</sub> in high CO<sub>2</sub> concentration in groundwater discharge that had an atmospheric signature (Gilfillan et al., 2017).

To evaluate the performance of the depleted noble gas signature of injected CO<sub>2</sub> as a fingerprint for monitoring storage sites, we must consider: (i) mixing of the CO<sub>2</sub> with the native gas in the reservoir and; (ii) degassing of noble gases from the formation water into the injected CO<sub>2</sub>. In Fig. 9[a], binary mixing of He and its isotopic ratio in captured CO<sub>2</sub> at TCM and Melkøya with natural gas from Melkøya is shown as a function of the content of injected CO<sub>2</sub> in natural gas. Mixing of the CO<sub>2</sub> with the native gas, which is enriched in noble gases, lowers the absolute concentrations at high CO<sub>2</sub> content (Fig. 9[a]). For the CO<sub>2</sub> from TCM, the isotopic ratio could enable additional and faster discrimination (Fig. 9[a]).

Simple binary mixing calculations neglect the interactions of the injected CO<sub>2</sub> with background fluids during storage and/or migration due to chemical and physical processes such as: formation water degassing, gas stripping, dissolution or adsorption, which have been observed and described in several studies, e.g. (Fanale and Cannon, 1971; Flude et al., 2017; Györe et al., 2017; Ju et al., 2020). To address the impact of formation water degassing in the storage formation, we calculate noble gas signatures in the CO<sub>2</sub> after equilibration with formation water, at different gas-water volume ratios,  $V_{\text{CO}_2}/V_{\text{H}_2\text{O}}$ . The calculations follow the derivation of phase partitioning based on Henry's law for liquid-gas systems described in Ballentine et al., 2002. Additionally, experimentally derived deviations of Henry coefficients for a high density CO<sub>2</sub>-H<sub>2</sub>O system are applied according to Warr et al., 2015. CO<sub>2</sub> densities are calculated from Ouyang (2011) and water densities are taken from NIST (2020). Typical noble gas concentrations in the formation water are estimated using the concentration reported in the Melkøya natural gas (sample #8, Table 1) and partitioning coefficients were calculated at realistic reservoir conditions (i.e. in-situ temperature, pressure and salinity) in the Snøhvit storage site.

Degassing of the formation water enriches the CO<sub>2</sub> with noble gases even at high  $V_{\text{CO}_2}/V_{\text{H}_2\text{O}}$ -ratios, as illustrated for He in Fig. 9[b]. This masks the depletion of noble gases and imprints the injected CO<sub>2</sub> with a crustal signature. The calculation illustrates how significantly depleted noble gas signatures may be altered during injection and migration.

Both calculations presented (Fig. 9), indicate that the initial signature and depletion in noble gas concentrations is only preserved or identifiable at extreme  $V_{\text{CO}_2}/V_x$ -ratios. For more realistic  $V_{\text{CO}_2}/V_{\text{H}_2\text{O}}$ -ratios, i.e. below the irreducible water saturation of the reservoir rock (Fig. 9[b]), the injected CO<sub>2</sub> will quickly inherit the noble gas signature of background reservoir fluids, making it distinct from atmospheric signature and imparting an identifiable natural fingerprint.

Seabed detection of a CO<sub>2</sub> leak then critically depends on effective baseline characterization of noble gas compositions in subsea gas seeps. Natural seeps are derived either from shallow biogenic gas or the breakdown of methane clathrates, and these are likely to have a composition distinct from the deep, radiogenic crust.

Aside from these model calculations, data and experience from the Melkøya site provide a practical illustration for targeted monitoring. Here, the CO<sub>2</sub> storage and the natural gas production reservoirs are within the same geological unit (the Stø Formation), but in different structural compartments (Halland et al., 2013). Routine measurements of noble gas content, revealing gradual depletion in the produced natural gas, could be used as a monitoring measure, if migration of injected CO<sub>2</sub> into the natural gas was suspected. Since it is a well characterized site, the necessary perturbation threshold may be decreased. Meanwhile, natural variation of the CO<sub>2</sub> content in produced gas renders the CO<sub>2</sub> concentration as tracer alone impractical. Here, semi-continuous measurements with the miniRuedi portable mass spectrometer could be applied to document variability in and between the various gas streams to estimate unintended, intra-formational mixing or leakage.

## 5. Conclusion

In this study we analysed the noble gases in the gas streams at two different Norwegian capture plants: Technology Centre Mongstad (TCM), a demonstration plant, and Melkøya, a large scale CCS site, capturing CO<sub>2</sub> naturally occurring in natural gas.

We observed that noble gas concentrations become depleted during the capture process. Two significant drivers affecting the noble gas concentrations in the captured CO<sub>2</sub> can be identified: the nature of the gas from which CO<sub>2</sub> is captured and the capture process itself, having site-specific properties. Concentrations of captured CO<sub>2</sub> span several orders of magnitude and the noble gas signature of the two plants are significantly different. Increasing the existing dataset with this study allows to infer specific noble gas concentrations for future projects.

The analytical approach developed here contributes to establishing a reliable sampling routine in capture facilities or before CO<sub>2</sub> injection to characterize the temporal evolution of noble gas concentrations of captured CO<sub>2</sub> and evaluate traceability at the storage site. The presented dataset also allows for investigation of the impact of processes such as foam development and applicability of Henry's law and forms a basis for comparison in future studies. While studies on noble gas solubilities in amine solvents in more controlled environments are necessary to quantify the single processes separately.

The recorded temporal variation does not preclude the value of noble gases as tracers since noble gas concentrations in capture streams are still significantly different, i.e. low, compared to geochemical reservoirs. Using mixing and noble gas partitioning calculations we show that the significant depletion in noble gas concentrations, together with degassing of noble gas enriched formation water, mean that the injected CO<sub>2</sub> will inherit the noble gas signature of the storage formation, even following the injection of significant CO<sub>2</sub> volumes. Any CO<sub>2</sub> leaked from the storage formation is thus likely to have a crustal noble gas signature, characteristic of the storage site, which can be targeted for monitoring. Seabed detection of a CO<sub>2</sub> leak then critically depends on effective baseline characterization of subsea gas seep noble gas compositions. Thus, more research on the change of noble gas fingerprints during migration in the subsurface and quantification of background concentrations is necessary before leakage detection using noble gases can be fully utilized. This work on noble gas signatures and temporal variation of capture streams should be an important step towards that goal.

## CRedit authorship contribution statement

**Ulrich W. Weber:** Writing - original draft, Investigation, Methodology, Formal analysis, Software, Data curation, Visualization, Conceptualization, Writing - review & editing. **Rolf Kipfer:**

Conceptualization, Methodology, Project administration, Writing - review & editing. **Edith Horstmann**: Investigation, Writing - review & editing. **Philip Ringrose**: Conceptualization, Project administration, Writing - review & editing. **Niko Kampman**: Software, Methodology, Writing - review & editing. **Yama Tomonaga**: Investigation, Formal analysis, Writing - review & editing. **Matthias S. Brennwald**: Methodology, Resources, Writing - review & editing. **Anja Sundal**: Investigation, Methodology, Conceptualization, Supervision, Project administration, Funding acquisition, Writing - review & editing.

### Declaration of Competing Interest

The authors report that they have no known competing interests that could have influenced this work.

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Paper III

# Techno-Economic Aspects of Noble Gases as Monitoring Tracers

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## Article

# Techno-Economic Aspects of Noble Gases as Monitoring Tracers

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**Abstract:** A comprehensive monitoring program is an integral part of the safe operation of geological CO<sub>2</sub> storage projects. Noble gases can be used as geochemical tracers to detect a CO<sub>2</sub> anomaly and identify its origin, since they display unique signatures in the injected CO<sub>2</sub> and naturally occurring geological fluids and gases of the storage site complex. In this study, we assess and demonstrate the suitability of noble gases in source identification of CO<sub>2</sub> anomalies even when natural variability and analytical uncertainties are considered. Explicitly, injected CO<sub>2</sub> becomes distinguishable from shallow fluids (e.g., subsea gas seeps) due to its inheritance of the radiogenic signature (e.g., high He) of deep crustal fluids by equilibration with the formation water. This equilibration also results in the CO<sub>2</sub> inheriting a distinct Xe concentration and Xe/noble gas elemental ratios, which enable the CO<sub>2</sub> to be differentiated from deep crustal hydrocarbon gases that may be in the vicinity of a storage reservoir. However, the derivation has uncertainties that may make the latter distinction less reliable. These uncertainties would be best and most economically addressed by coinjection of Xe with a distinct isotope ratio into the CO<sub>2</sub> stream. However, such a tracer addition would add significant cost to monitoring programs of currently operating storage projects by up to 70% (i.e., from 1 \$US/t to 1.7 \$US/t).



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**Keywords:** carbon capture and storage; monitoring and verification; noble gases; leakage detection; inherent distinctiveness; tracer addition; cost calculation

## 1. Introduction

Measurement, monitoring, and verification (MMV) programs are an essential part of the safe operation of geological CO<sub>2</sub> storage (GCS or CCS, when including capture) project [1,2]. On the one hand, a robust MMV strategy helps to ensure long-term storage security, to meet climate change mitigation goals, and to manage public acceptance [1]. On the other hand, for scaling CCS to climate relevant amounts of CO<sub>2</sub> stored, the associated cost of such a strategy cannot jeopardize the economic viability of a project that is heavily dependent on carbon pricing [3].

Chemical changes and tracers can be monitored at storage sites, potentially enabling detection of a CO<sub>2</sub> leak and identification of the source of observed anomalies [1,4]. Noble gases are one chemical tracer group that has received attention due to their key properties of being inert and having a large number of isotopes that can be measured with high precision [5,6]. This makes them safe to utilize in industrial processes and their use does not have additional negative environmental consequences. The concentrations of He, Ne, Ar, Kr, Xe, and their isotopic ratios constitute the noble gas signature of a fluid. This practically labels most environmental reservoirs with an identifiable atmospheric [7], crustal (radiogenic) [8], or mantle [9] signature [10]. Further, injected CO<sub>2</sub> from various capture processes (anthropogenic) has an inherent noble gas signature, which depends on the CO<sub>2</sub> source and capture process [11–13].

The conservative behavior of noble gases and the knowledge of the baseline noble gas signatures of the storage system allows end-member mixing calculations to be performed, such as those used in a study that refused an alleged leak from a CO<sub>2</sub> storage site [14].

Further, in CO<sub>2</sub> injection for enhanced oil recovery (EOR), changes in the noble gas signature of the produced fluids quantified the contribution of the injected CO<sub>2</sub> [15–17]. It is also possible to label the injected CO<sub>2</sub> with deliberately added noble gases to distinguish the signature of the injected CO<sub>2</sub> further [15,18]. However, this has only been conducted in small-scale injection experiments, but allowed for identification of the CO<sub>2</sub> gas plume distribution and of mixing and degassing processes, e.g., [19].

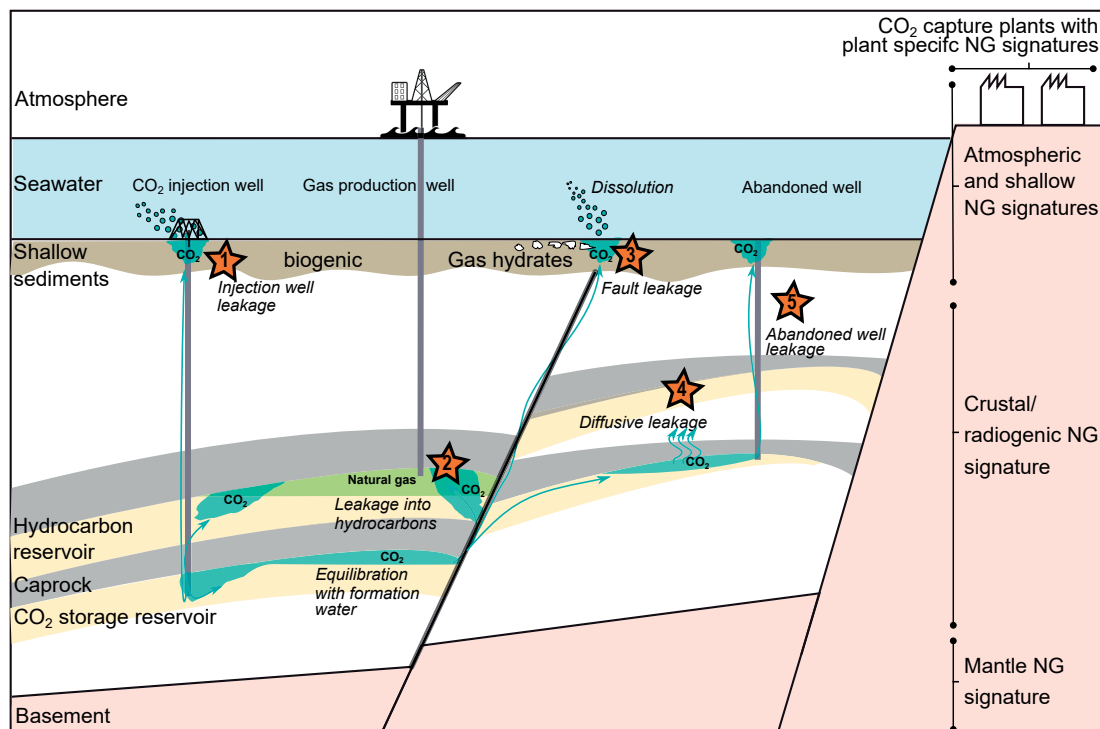
In the study by Roberts et al. [18], the addition of noble gas tracers is discussed from a practicality and cost perspective for large-scale storage. Tracer addition was analyzed to differentiate the noble gas signature of the injected, and eventually, leaking CO<sub>2</sub> from the background signatures of seawater and atmosphere. They conclude that He and <sup>124,129</sup>Xe isotopes are most suitable as added tracers with costs in the order of 100–100,000 £/MtCO<sub>2</sub>, similar to earlier results by Nimz et al. [15].

In [12,13], we outlined that the injected CO<sub>2</sub> is likely to inherit a radiogenic noble gas signature from the storage formation waters through equilibration or mixing with native formation gases. The calculation based on phase partitioning data for a high-pressure CO<sub>2</sub>-H<sub>2</sub>O-system [20] led to the hypothesis that injected CO<sub>2</sub> becomes differentiable from atmospheric signatures without the need of adding tracers.

The altered, radiogenic signature of the injected CO<sub>2</sub> is similar to natural hydrocarbons [21]. Hydrocarbon reservoirs are often found in the vicinity of a number of active or suggested CO<sub>2</sub> storage sites, e.g., [22–24]. A leak into such hydrocarbon reservoirs may not have the environmental impact of a leak to the seabed, but the contamination of these resources can have significant economic consequences. Further, if the CO<sub>2</sub> was to be fed back into the atmosphere, subsequent to gas or oil production, the climate mitigation value of a CCS project would be reduced. Therefore, there is the need to expand the evaluation of the distinctiveness of noble gas signatures and tracer addition to include the discrimination of CO<sub>2</sub> and hydrocarbon gases.

There are several possible scenarios of how leakage could occur to the atmosphere or seabed or into hydrocarbon reservoirs [25]. An overview of some possible pathways that may result in varying exchange of the injected CO<sub>2</sub> with the storage site fluids and mixture with different background reservoirs is shown in Figure 1. An injection well leak, case 1 in Figure 1, could leave the CO<sub>2</sub> with its initial composition; meanwhile, cases 2, 3, 4, and 5 would likely lead to significant interaction of the CO<sub>2</sub> with crustal fluids. Therefore, including the phase partitioning between the injected CO<sub>2</sub> and formation water data derived in [20] is an essential addition in the assessment of noble gas tracers, both from a technical and economic perspective.

In this work, we aim to validate the hypothesis of the inherent differentiability of the injected CO<sub>2</sub> from the atmospheric signatures quantitatively drawn in [12]. We will conduct calculations based on current analytical capabilities for noble gases and the natural variability of noble gas signatures. In the same way, we evaluate distinctiveness to other environmental signatures, i.e., natural gas and gas hydrates, that have to be considered in the leakage scenarios 2–5 in Figure 1. Then, we derive the necessary amounts and the associated cost for tracer addition to increase distinctiveness between the injected CO<sub>2</sub> and hydrocarbons, i.e., natural gas. Finally, we discuss the practical and economic roles of noble gases in a monitoring scheme and the implications for the viability of a storage project.



**Figure 1.** Overview sketch of a CO<sub>2</sub> storage site with areas typically attributed to a type of noble gas (NG) signature [10]. CO<sub>2</sub> will have a different NG signature for different plant types, such as postcombustion, natural gas processing, or oxyfuel [11,12]. Possible leakage pathways are (1) injection well leakage, (2) migration into and contamination of hydrocarbon reservoirs that may subsequently be produced, (3) fault leakage, (4) diffuse leakage, and (5) leakage through an abandoned well. Leaking CO<sub>2</sub> may enter the atmosphere or dissolve in seawater.

## 2. Materials and Methods

### 2.1. Background Concentrations

Noble gas tracers have widespread application in deciphering physical and chemical processes in geosciences [10] since they are only influenced by physical processes. There are three main groups of noble gas signatures in the environment, which are of atmospheric [7], crustal [8], or mantle [9] character and allow researchers to attribute the source of a fluid. In practice, these categories in themselves can have wide isotopic concentration ranges or be mixtures derived during the history of origin of a fluid. Characterizing the background fluids of a storage site is key for the applicability of noble gases as tracers.

Here, we collect and discuss the known signatures from samples relevant to a possible storage site in the North Sea (Table 1). This is due to the topicality of the Norwegian large-scale storage project ‘Longship’, which is currently under development [26]. Additionally, in this project, a contamination of the stratigraphically overlying Troll gas and oil field could be considered a risk [27]. Analogue studies may be used and discussed where samples are not available. These signatures may have to be adapted for other sites but reflect typical continental shelf settings.

For natural gas, sample analyses for the North Sea are currently available for the Sleipner Vest and the Magnus fields [28,29]. The results show a typical crustal, radiogenic character, derived from the accumulation of <sup>4</sup>He, <sup>21</sup>Ne, and <sup>40</sup>Ar through radioactive decay of the elements K, U, and Th in the rocks [8]. The radioactive accumulation is a function of time and the content of radioactive elements in the rock. The radiogenic signature acquires an atmospheric gas component from the in situ formation water that was in atmospheric equilibrium during sedimentation, or meteoric recharge. The additional amounts of stripped gas then depend on the gas/water volume ratio,  $V_g/V_w$ , and if the hydrocarbon system is closed or open, allowing for significant gas volumes to migrate through a reservoir [28].

**Table 1.** Observed noble gas concentrations for different environmental fluids. Natural gas for He, Ne, and Ar compiled from the North Sea Sleipner and Magnus Fields in [28,29], and Kr and Xe from the Sleipner Field [28]. Natural, geologic CO<sub>2</sub> compiled from [30,31]. Sediment values from the South Pacific Ocean [32] and the Mediterranean Ridge for He [33]. Gas hydrates from [34]. Seawater concentrations after [35] (assuming a temperature of 7.5 °C and a salinity of 34.2 g/L). Atmospheric values from [7]. Captured CO<sub>2</sub> from several sites [11–13]. In cm<sup>3</sup><sub>STP</sub>/cm<sup>3</sup><sub>STP</sub>, if not otherwise stated. Rounded to nearest tenth asides atmosphere.

	He	Ne	Ar	Kr	Xe
Natural Gas/Oil	1.2E-05–1.3E-04	7.0E-07–2.7E-08	1.1E-05–4.1E-05	4.1E-09–5.2E-09	1.3E-09–1.6E-09
Natural, geologic CO <sub>2</sub>	1.0E-04–1.0E-02	7.0E-08–1.8E-06	1.5E-05–2.7E-05	1.0E-10–1.0E-08	5.0E-12
Gas Hydrates	7.0E-10–9.0E-10	2.5E-09–6.2E-08	3.5E-05–5.3E-04	1.8E-08–3.0E-07	2.7E-09–9.4E-08
Seafloor Sediments (cm <sup>3</sup> <sub>STP</sub> /g)	1.0E-04–1.0E-02	5.0E-09–5.0E-07	1.0E-05–1.0E-08	5.0E-08–1.5E-09	8.0E-09–1.7E-08
Seawater (cm <sup>3</sup> <sub>STP</sub> /g)	4.0E-08	5.7E-09	1.1E-06	8.5E-08	1.1E-08
Atmosphere	5.24E-06	1.82E-05	9.34E-03	1.13E-06	8.7E-08
Captured CO <sub>2</sub>	2.3E-09–2.9E-06	5.9E-11–4.3E-07	3.7E-10–1.4E-04	3.6E-12–6.3E-09	1.1E-13–1.9E-09

Natural, geologic CO<sub>2</sub> shows dominantly magmatic, and hence, mantle signatures with subsequent equilibration with radiogenic formation water. The values in Table 1 are from large natural CO<sub>2</sub> systems in the US [30,31]. Natural CO<sub>2</sub> in the North Sea context is typically a minor constituent of natural gas accumulations, e.g., [22], and would therefore have very similar noble gas signatures as the associated hydrocarbons.

The values for both natural gas and natural, geologic CO<sub>2</sub> depict that the noble gas concentration within what is considered a radiogenic signature can vary by orders of magnitude (see Table 1). For the ‘Longship’ project, the most relevant radiogenic signature to compare to with respect to traceability of CO<sub>2</sub> is storage reservoir formation water and gas and oil in the Troll Field stratigraphically overlying the storage formation. Even though the Troll gas and oil reservoirs are shallower than in the Magnus and Sleipner fields, the age and the proposed origin of the Troll hydrocarbons in the Oseberg area [36] would suggest that noble gas signatures in the Troll field are similar to those in Table 1.

Close to the seabed, gas hydrates may occur. Only total gas concentration, not isotopic composition, have been analyzed for these [34]. Those samples were collected outside the coast of Oregon, US, and showed a quite specific fractionation pattern with preferential incorporation of heavier noble gases and suppression of the lighter ones. This fractionation process should be independent of the location, making the concentrations applicable for the North Sea if gas hydrates were to be found.

Analysis of the dissolved noble gas distribution in the pore-water of shallow, unconsolidated sediments are relatively rare [32,33,37] and, for the North Sea, there is no dataset available. Sediment pore-water concentrations are dependent on the temperature during sedimentation and if there are leakage sites, e.g., shallow biogenic gas or deep fluid release, such as black smokers, nearby. The data from [32,33,37] in Table 1 has to be seen in the context of plate boundaries and is therefore not representative for the continental crust of the North Sea. However, there have been methane leakages above the Troll field in the past [38], which could have left a minor radiogenic component in the pore-water signature.

Seawater, if not in the vicinity of specific fluid releases, is typically air equilibrated water at a given temperature and salinity [35]. This means atmospheric gas, including noble gases, is dissolved based on the solubility of the respective gas species at these conditions in water. In case there are seepages, ocean currents may redistribute them quickly, so anomalies can be local. The atmosphere is typically well mixed and has a specific noble gas signature [7].

The noble gas signature of captured CO<sub>2</sub> has been analyzed for several capture plants in Norway [12,13] and other countries [11]. Noble gas concentrations are typically low and the isotopic signatures are either airlike for plants with combustion prior to capture (e.g., waste incineration) or natural-gas-like (e.g., natural gas processing). For captured CO<sub>2</sub>,

the observed range spans several orders of magnitude. Captured CO<sub>2</sub> from oxyfuel plants, for example, are significantly enriched in Kr and Xe [6].

With regards to isotopic ratios, there are the three main signatures and fluids that represent mixtures of these to various degrees. Typical values for the mainly affected isotopes are shown in Table 2.

Noble gas ratios associated with hydrocarbons are, as previously discussed for concentrations, dependent on the geological setting of a reservoir and the provenance of the hydrocarbons. In Table 2, isotopic ratios are shown for the North Sea [28]. However, the <sup>3</sup>He/<sup>4</sup>He and <sup>40</sup>Ar/<sup>36</sup>Ar ratio especially can vary significantly, e.g., natural gas from Snøhvit has a He-ratio an order of magnitude lower [12].

**Table 2.** Isotopic ratios for the main signatures: atmospheric; crustal, hence radiogenic; and mantle. Atmospheric values from [7]. Natural gas from the Sleipner field [28]. Mantle data from [9].

	<sup>3</sup> He/ <sup>4</sup> He (R/R <sub>A</sub> )	<sup>21</sup> Ne/ <sup>22</sup> Ne	<sup>40</sup> Ar/ <sup>36</sup> Ar	<sup>86</sup> Kr/ <sup>84</sup> Kr	<sup>132</sup> Xe/ <sup>130</sup> Xe
Atmospheric Signature	1	0.029	296	0.303	6.61
Crustal signature	~0.1	~0.033	~455	~0.303	~6.61
Mantle signature (MORB)	8	0.06	~30,000	-	-

For captured CO<sub>2</sub>, the ratios are dependent on the source of the CO<sub>2</sub> and if combustion has taken place prior to capture, e.g., at heat and power plants. Combustion introduces noble gases from the air shifting ratios towards atmospheric values. At natural gas processing sites, the radiogenic ratios are maintained [12]. However, one has to consider that the CO<sub>2</sub> can undergo interaction with, for example, in situ formation water or gases, subsequently altering the noble gas fingerprint, as we discuss next.

## 2.2. Phase Partitioning

Following injection, the equilibration of the injected CO<sub>2</sub> with the formation water of the storage reservoir will significantly modify its composition, especially given that captured and injected CO<sub>2</sub> will be significantly depleted in noble gases [12]. We calculate this phase partitioning by applying Henry's law following the derivation for the thermodynamic conditions governing in the crust in [39]. The gas concentration *c* of a gas *i* in the gas phase calculates to

$$c_{i,g} = c_{i,T} \left( \frac{22400T\rho_{H_2O}}{18 \cdot 273 \frac{\gamma_i}{\phi_i} K_{i,CO_2-H_2O}} \frac{V_{H_2O}}{V_{CO_2}} + 1 \right)^{-1}, \quad (1)$$

with the total concentration *c<sub>T</sub>* of gas *i*; water density  $\rho_{H_2O}$  at system pressure; temperature *T*; activity  $\gamma_i$ ; and fugacity  $\phi_i$  of the gas at system pressure, temperature, and volume of water CO<sub>2</sub>, *V<sub>H<sub>2</sub>O</sub>*, and *V<sub>CO<sub>2</sub></sub>*, respectively.

Values of  $K_{i,H_2O}$ ,  $\gamma_i$ , and  $\phi_i$  are collected in [39]. However, Henry's constants  $K_i$  of noble gases were found to deviate significantly for a high-density CO<sub>2</sub>-H<sub>2</sub>O system [20]. Warr et al. [20] experimentally derived deviation factors  $\kappa_i$  for all noble gases besides Ne and Rn. This correction allows calculation of the deviation of Henry's constant with gas-specific constants in the dependency of CO<sub>2</sub> density:

$$K_{i,CO_2-H_2O} = \kappa_i K_{i,H_2O} = \left( \frac{a_i \rho_{CO_2}^2 + b_i \rho_{CO_2} + c_i}{100} + 1 \right) K_{i,H_2O}. \quad (2)$$

$K_{i,H_2O}$  is Henry's constant at a given temperature in units of pressure for a low-pressure air-water system. The upper limit for density in the experiments of [20] was 656 kg/m<sup>3</sup>. Though explicitly advised against, we also apply this deviation for densities up to 700 kg/m<sup>3</sup> due to the lack of data.

The densities in Equations (1) and (2) are also functions of temperature and pressure, which can be expressed as gradients of depth. Geothermal and pressure gradients vary in different geological settings. Here, we use 30 K/km and 10.18 MPa/km. We derive the densities for CO<sub>2</sub> from [40] and for H<sub>2</sub>O from [41].

Since Equation (1) is a function of the volume ratio  $V_{H_2O}/V_{CO_2}$ , phase partitioning can be calculated independent of actual storage site volume. In this work, we derive phase-partitioned values at the ratio of maximum saturation  $S_{max}$  of CO<sub>2</sub> for residual trapping in a reservoir rock containing CO<sub>2</sub> and water. The CO<sub>2</sub> saturation was found experimentally to be between 13 and 92% for several reservoir rock samples, with a mean of 61% [42], which is subsequently used.

The total concentration of a gas in the system is derived from the sum of the product of concentration in the single phases and their volumes, hence,

$$c_{i,T} = c_{i,CO_2,inj} \cdot V_{CO_2} + c_{i,H_2O} \cdot V_{H_2O}, \quad (3)$$

where  $c_{i,CO_2,inj}$  are the inherent concentrations in captured CO<sub>2</sub> (see Table 1). There are currently no formation water analyses on noble gases for the North Sea. Therefore, we derive the formation water concentrations,  $c_{i,H_2O}$ , assuming natural gas from the Sleipner field in [28] had been in equilibrium with formation water. For the calculation of tracer addition, the concentrations in  $c_{i,CO_2,inj}$  can be altered such that Equation (1) results in the desired  $c_{i,g}$ .

### 2.3. Distinctiveness

The distinctiveness of the noble gas signature is constrained by analytical capabilities and natural variability. These have to be considered when analyzing the reliability of mixing calculations. In [18], it is assumed that “10 times the detectable perturbation above background levels are required for reliable tracer detection in the atmosphere or seawater”, hence, a leak would then be identified. As discussed in Section 2.1, the signatures in the atmosphere and seawater that were analyzed in [18] can be reasonably assumed to be fixed.

Tables 1 and 2 show that this is not the case for hydrocarbons and gas hydrates, such that the natural variability has to be considered to further constrain the distinctiveness. We use the values in [28] to derive the natural variability that can be expected for a gas field. The resulting ranges are smaller than observed in the Magnus Field [29]; however, it appears that analytical capabilities have increased significantly, such that the samples from [28] are likely to reflect state-of-the-art precision and accuracy.

Our criterion for being distinct is that the resulting concentration in a mixture of 90% background fluid and 10% equilibrated CO<sub>2</sub> has to be larger than the natural variability plus the  $3\sigma$ -interval of the typical measurement error in [28].

## 3. Results

### 3.1. Equilibration with Formation Water

The phase partitioning of injected CO<sub>2</sub> with the formation water leads to a significant change of the initially depleted signature of the captured CO<sub>2</sub>. The results of the calculation at 2000 m depth following Section 2.2 for the respective isotopes and ratios are shown in Table 3. Ne is not further considered since there are no correction terms for a CO<sub>2</sub>-H<sub>2</sub>O-system available.

Injected CO<sub>2</sub> acquires a specific signature. With the high He ( $\sim 3.90E-05 \text{ cm}^3_{STP}/\text{cm}^3_{STP}$ ), it may be considered a radiogenic signature; however, the correction term for the solubilities for a CO<sub>2</sub>-H<sub>2</sub>O-system (Equation (2)) affects each gas species individually. For example, the phase partitioning leads to a signature that is  $\sim 500\%$  different compared to natural gas in Xe. It is also very different compared to atmosphere,  $\sim 750\%$  in He, and compared to gas hydrates  $\sim 5E+07\%$  in He Table 3.

Results are calculated both for the highest and lowest values in captured CO<sub>2</sub> (see Table 1). The concentrations in the injected CO<sub>2</sub> are most influential for Ar results with a resulting  $\sim 50\%$  difference for <sup>36</sup>Ar.



These values can be compared to the analytical uncertainty of an elements measurement and the natural variability in natural gas for the results of the Sleipner field [28], which can be as high as 45%, as stated in Table 3.

**Table 3.** Noble gas concentrations in  $\text{cm}^3_{\text{STP}}/\text{cm}^3_{\text{STP}}$  and isotopic ratios after equilibration with formation water for low and high concentrations in captured  $\text{CO}_2$ , as in Table 1. Analytical uncertainty and natural gas variability from the Sleipner field in [28]. Concentrations and ratios are relative to the respective background fluids; the stated ranges are for  $c_{g,\text{low},S_{\text{max}}}$  and  $c_{g,\text{high},S_{\text{max}}}$ , respectively.

	$c_{g,\text{low},S_{\text{max}}}$ <b>Low Captured</b> <b><math>\text{CO}_2</math> Values</b>	$c_{g,\text{high},S_{\text{max}}}$ <b>High Captured</b> <b><math>\text{CO}_2</math> Values</b>	<b>Analytical</b> <b>Uncertainty</b>	<b>Variability</b> <b>in Natural</b> <b>Gas</b>	$c_{g,S_{\text{max}}}$ <b>rel.</b> <b>to Average</b> <b>Natural Gas</b>	$c_{g,S_{\text{max}}}$ <b>rel.</b> <b>to Atmosphere</b>	$c_{g,S_{\text{max}}}$ <b>rel.</b> <b>to Hydrates</b>
He	3.90E-05	3.92E-05	2%	8%	62–63%	744–749%	4,900,000%
$^4\text{He}$	3.90E-05	3.92E-05	2%	8%	62–63%	744–749%	-
$^3\text{He}$	5.86E-12	6.49E-12	3%	35%	62–68%	80–88%	-
$^3\text{He}/^4\text{He}$	1.50E-07	1.65E-07	3%	13%	104–115%	11–12%	-
Ar	5.22E-05	7.09E-05	2%	30%	166–225%	1%	52–71%
$^{36}\text{Ar}$	1.13E-07	1.75E-07	1%	45%	166–258%	1%	-
$^{40}\text{Ar}$	5.21E-05	7.07E-05	2%	30%	166–225%	1%	-
$^{40}\text{Ar}/^{36}\text{Ar}$	4.63E+02	4.05E+02	1%	5%	99–87%	156–137%	-
Kr	1.06E-08	1.16E-08	2%	18%	239–262%	1%	13–14%
$^{84}\text{Kr}$	8.12E-09	8.89E-09	2%	18%	239–261%	1%	-
$^{86}\text{Kr}$	2.46E-09	2.69E-09	1%	17%	239–262%	1%	-
$^{86}\text{Kr}/^{84}\text{Kr}$	3.03E-01	3.03E-01	1%	1%	100%	99%	-
Xe	6.36E-09	6.67E-09	5%	10%	458–480%	7–8%	13%
$^{124}\text{Xe}$	6.37E-12	7.46E-12	3%	8%	458–536%	8–9%	-
$^{126}\text{Xe}$	5.66E-12	6.67E-12	3%	11%	458–540%	7–9%	-
$^{128}\text{Xe}$	1.16E-10	1.38E-10	3%	17%	458–544%	7–8%	-
$^{129}\text{Xe}$	1.68E-09	1.98E-09	3%	11%	458–540%	7–9%	-
$^{130}\text{Xe}$	2.56E-10	3.03E-10	3%	12%	458–541%	7–9%	-
$^{131}\text{Xe}$	1.36E-09	1.60E-09	3%	10%	458–539%	7–9%	-
$^{132}\text{Xe}$	1.71E-09	2.02E-09	3%	9%	458–540%	7–9%	-
$^{134}\text{Xe}$	6.63E-10	7.82E-10	3%	11%	458–540%	7–9%	-
$^{136}\text{Xe}$	5.64E-10	6.65E-10	3%	11%	458–540%	7–9%	-
$^{124}\text{Xe}/^{130}\text{Xe}$	2.49E-02	2.46E-02	5%	9%	101–100%	106–105%	-
$^{126}\text{Xe}/^{130}\text{Xe}$	2.21E-02	2.20E-02	5%	3%	101%	101–101%	-
$^{128}\text{Xe}/^{130}\text{Xe}$	4.52E-01	4.55E-01	5%	5%	101–102%	96–96%	-
$^{129}\text{Xe}/^{130}\text{Xe}$	6.55E+00	6.54E+00	5%	1%	101%	101%	-
$^{131}\text{Xe}/^{130}\text{Xe}$	5.31E+00	5.30E+00	5%	2%	101%	102%	-
$^{132}\text{Xe}/^{130}\text{Xe}$	6.68E+00	6.67E+00	5%	1%	101%	101%	-
$^{134}\text{Xe}/^{130}\text{Xe}$	2.59E+00	2.58E+00	5%	1%	101%	101%	-
$^{136}\text{Xe}/^{130}\text{Xe}$	2.20E+00	2.20E+00	5%	1%	101%	101%	-

### 3.2. Tracer Addition

Needed concentrations in the injection stream to achieve additional distinction range from  $1\text{E}-11 \text{ cm}^3_{\text{STP}}/\text{cm}^3_{\text{STP}}$  for some Xe isotopes to  $1\text{E}-03 \text{ cm}^3_{\text{STP}}/\text{cm}^3_{\text{STP}}$  for elemental He. The results for the amounts of a specific gas isotope needed for deliberate tracer addition are shown in Table 4. Calculations are conducted in order to increase distinctiveness of the injected, equilibrating  $\text{CO}_2$  from natural gas, following the description in Section 2.2. The results fulfill the condition set in Section 2.3. Then, the necessary concentrations

that the injected CO<sub>2</sub> needs to be labeled with to achieve the given concentrations after equilibration are given.

The necessary concentrations in the injected CO<sub>2</sub> are scaled up to volumes of the respective tracer gas needed in a 1MtCO<sub>2</sub>/a storage project, depicting the large range of concentrations needed for the different gases. These volumes range from 1E+01 to 1E+08 l/a (Table 4). From the amounts needed, the cost of an isotope addition is derived to a wide range of 0.7 to 37,000 \$US/tCO<sub>2</sub> for the different gases. For reference, the price calculation is performed to fulfill the method used in [18] (see Section 2.3). Here, tracer addition would be up to 3 orders of magnitude cheaper.

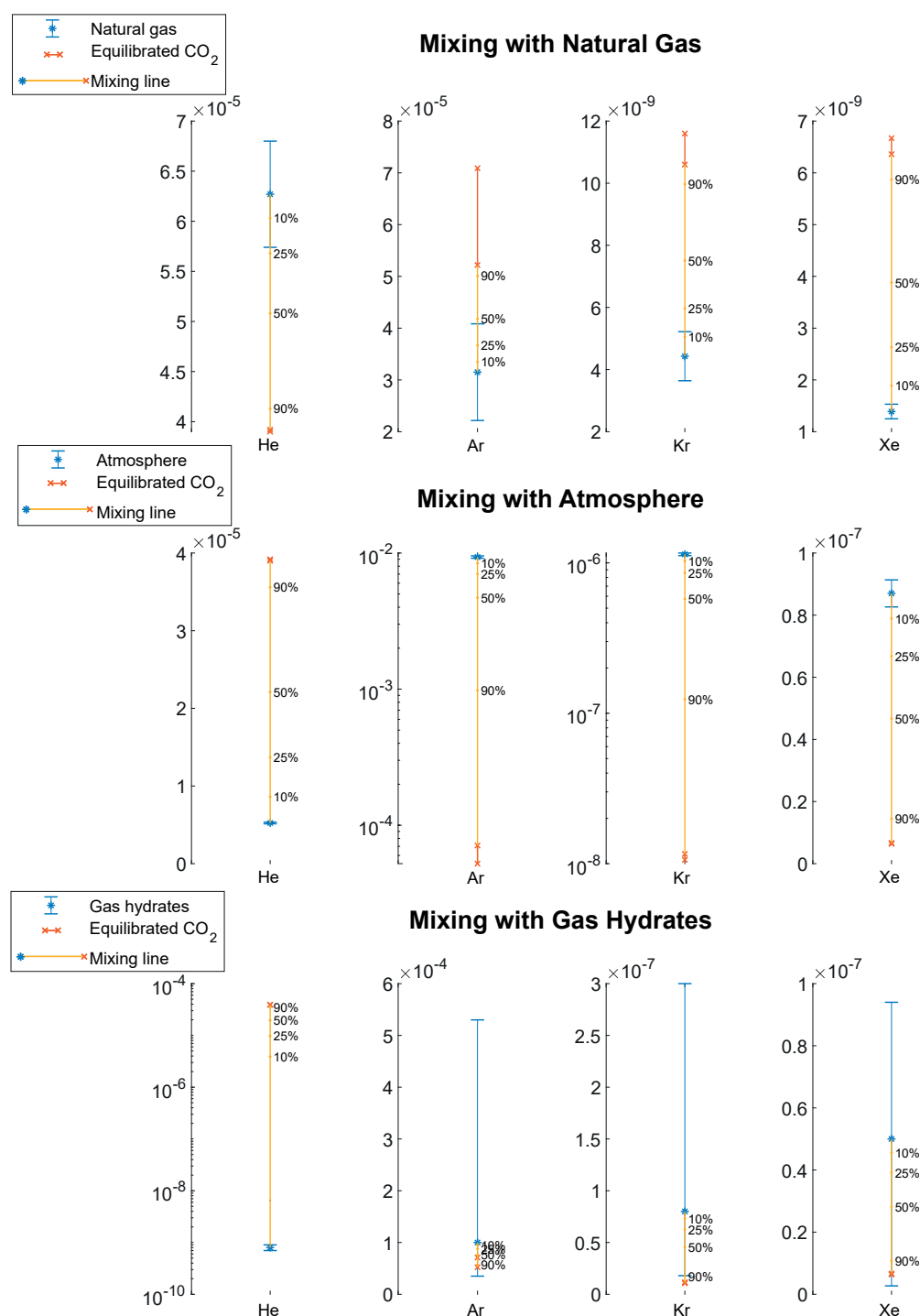
**Table 4.** Necessary noble gas concentrations in cm<sup>3</sup><sub>STP</sub>/cm<sup>3</sup><sub>STP</sub> and isotopic ratios to fulfill the detection condition described in Section 2.3 both in the equilibrated and the injected CO<sub>2</sub>. For isotopic ratios, calculations are conducted for the isotope in the numerator of the ratio. As shown in Section 3.1, the distinctiveness condition for Xe and its isotopes is inherently met in our calculations. For Xe ratios, a concentration of 1.50E-11 <sup>130</sup>Xe inherent in the injected CO<sub>2</sub> is assumed. The volume is calculated for 1MtCO<sub>2</sub>/a storage project, and the associated cost for a tracer addition is derived. For comparability, the cost is additionally derived with the method in [18] and gas prices as in [18], where applicable. Exchange rate used for prices in [18]: £ = 1.3·\$US.

	Nec. Conc./ Ratio in Equilibrated CO <sub>2</sub>	Nec. Conc. in Injected CO <sub>2</sub>	Nec. Volume in a 1MtCO <sub>2</sub> /a Project (l/a)	Gas Price (\$US/l)	Cost (\$US/tCO <sub>2</sub> )	Cost; Method as in [18] (\$US/tCO <sub>2</sub> )	Gas Price Source
He	1.53E-04	1.26E-03	6.43E+08	57.2	37,000	18,000	[18]
<sup>3</sup> He	3.02E-11	2.72E-10	1.39E+02	3800	0.69	750	[18]
<sup>3</sup> He/ <sup>4</sup> He	7.72E-07	2.74E-10	1.40E+02	3800	0.69	0.07	[18]
Ar	1.43E-04	7.60E-04	3.88E+08	64.38	32,000	13,400	[18]
<sup>36</sup> Ar	3.91E-07	2.09E-06	1.07E+06	1000	1066	450	Shell
<sup>36</sup> Ar/ <sup>40</sup> Ar	3.79E-03	1.17E-06	5.97E+05	1000	597	23	Shell
Kr	1.50E-08	3.60E-08	1.84E+04	107	2.55	3.16	[18]
<sup>86</sup> Kr	3.14E-09	5.55E-09	2.83E+03	1490	5.48	10.16	[18]
<sup>86</sup> Kr/ <sup>84</sup> Kr	4.25E-01	1.08E-08	5.51E+03	1490	10.67	0.01	[18]
Xe	4.89E-09	Condition met inherently		340	-	3.13	[18]
<sup>124</sup> Xe/ <sup>130</sup> Xe	8.48E-02	9.70E-11	4.95E+01	28,554	1.84	0.00026	[18]
<sup>126</sup> Xe/ <sup>130</sup> Xe	6.21E-02	6.48E-11	3.31E+01	17,600	0.76	0.00014	[18]
<sup>128</sup> Xe/ <sup>130</sup> Xe	1.35E+00	1.45E-09	7.40E+02	-	-	-	
<sup>129</sup> Xe/ <sup>130</sup> Xe	1.63E+01	1.58E-08	8.06E+03	330	2.66	0.0062	Shell
<sup>131</sup> Xe/ <sup>130</sup> Xe	1.44E+01	1.48E-09	7.55E+02	1650	1.25	0.0025	Shell
<sup>132</sup> Xe/ <sup>130</sup> Xe	1.66E+01	1.60E-08	8.16E+03	2200	17.96	638	Shell
<sup>134</sup> Xe/ <sup>130</sup> Xe	6.50E+00	6.33E-09	3.23E+03	4585	19.25	0.0044	[18]
<sup>136</sup> Xe/ <sup>130</sup> Xe	5.55E+00	5.43E-09	2.77E+03	2200	6.09	0.0014	Shell

## 4. Discussion

### 4.1. Inherent Distinctiveness

The phase-partitioning calculations show that inherited noble gas signatures of injected CO<sub>2</sub> are significantly distinct compared with all background signatures, given the presented analytical uncertainty and database (Table 3). This is further demonstrated when mixing He, Ar, Kr, and Xe concentrations in the CO<sub>2</sub> with the respective gas concentrations in natural gas, atmosphere, and gas hydrates (yellow lines in Figure 2).



**Figure 2.** Mixing of the equilibrated CO<sub>2</sub> with background concentrations in natural gas, atmosphere, and gas hydrates in (cm<sup>3</sup><sub>STP</sub>/cm<sup>3</sup><sub>STP</sub>). For seawater, gas-specific solubilities have to be applied. The range of equilibrated CO<sub>2</sub> is the orange line, with the values as stated in Table 3. Mixing is calculated for the lower of these values. Background concentrations are shown with error bars (blue)—being dominated by the natural variability for natural gas and gas hydrates, and the analytical uncertainty for the atmosphere.

In the case of equilibrated CO<sub>2</sub> mixing with natural gas, case 2 in Figure 1, Xe is most distinct and would allow identification of injected CO<sub>2</sub> in gas mixtures at percentages of CO<sub>2</sub> as low as 3% (Figure 2). For He, Ar and Kr distinctiveness is worse. This is mainly caused by the natural variability in the natural gas (blue error bars in Figure 2). Further,

for Ar and Kr, the range of the concentrations in the equilibrated CO<sub>2</sub> is relatively large, resulting from the concentration range in the captured CO<sub>2</sub> (orange line in Figure 2).

Even though different to the natural gas, the equilibrated signature of injected CO<sub>2</sub> exhibits some characteristics of a radiogenic signature. Primarily, high He makes the signature very distinct compared to the atmosphere and gas hydrates (Figure 2). For mixing of injected and equilibrated CO<sub>2</sub> with the atmosphere, all gases are significantly different (note the logarithmic scale for Ar and Kr in the second row of Figure 2). He will be most reliable since He concentration is the only gas that is higher in the equilibrated CO<sub>2</sub> than in the atmosphere.

For seawater, the assumption can be made that the distinctiveness will be the same as for an atmospheric signature, considering that the same Henry's constants would be applied to the dissolution of noble gases for both air and leaking CO<sub>2</sub>.

The very distinct depletion of He in gas hydrates allows unambiguous identification of an injected and equilibrated CO<sub>2</sub> component in a mixture of these two components (note the logarithmic scale for He in the third row of Figure 2). The other gases exhibit large natural variability and therefore do not add distinctiveness.

#### 4.2. Limitations of the Method

##### 4.2.1. Calculation Method

In the calculations of phase partitioning, we calculated the specific solubility in a CO<sub>2</sub>-H<sub>2</sub>O-system using the correction term of [20] (Equation (2)). For deriving the formation water concentrations of noble gases in the storage reservoir—currently not directly measured—we assumed equilibrium with the analyzed natural gas. Here, we used solubilities for a high-pressure H<sub>2</sub>O-system, i.e., not applying  $\kappa_i$  in Equation (2). Such specific correction terms for the noble gas solubility in a CH<sub>4</sub>-CO<sub>2</sub>-system have yet to be derived. The CO<sub>2</sub>-solubility correction, i.e., the preferential partitioning into the CO<sub>2</sub> phase, is exactly what makes Xe values in particular differ significantly (~500% in Table 3). Deriving correction terms for a high-pressure CH<sub>4</sub>-CO<sub>2</sub>-system may alter the concentrations and lead to the signatures that the injected CO<sub>2</sub> adopts to be less or more distinct. Further, impurities in the CO<sub>2</sub> injection stream could impact the applicability of solubilities for a pure CO<sub>2</sub>-H<sub>2</sub>O-system; however, such deviations are anticipated to be minor given the relatively pure nature of injected CO<sub>2</sub>. For example, the injected CO<sub>2</sub> at the Sleipner storage site has a CH<sub>4</sub> constituent of only 1–2% [22].

We further assumed that phase partitioning is the only process influencing the signature before mixing. Mixing with native formation gases, such as minor CH<sub>4</sub> accumulations, could alter the mixtures significantly, i.e., including a signature of natural gas. Thereby, the injected CO<sub>2</sub> would be more similar to natural gas, reducing distinctiveness towards it. The inclusion of the radiogenic signature from native formation gases would, however, further increase distinctiveness towards shallow signatures.

##### 4.2.2. Leakage Scenarios

Reaching initial equilibrium with the formation water may depend on the type of leakage. The later a leak occurs after injection, the more likely equilibrium is achieved. For “catastrophic” leakages—e.g., at the injection well—the CO<sub>2</sub> could stay in its depleted state (case (1) in Figure 1). Such a leak can be detected based on a suit of other geophysical and geochemical tools that are installed along the well [1]. The depleted noble gas concentrations could, however, be used for leakage attribution. For other advective leakage types—e.g., cases 2, 3, 4, and 5 in Figure 1—the CO<sub>2</sub> will likely have equilibrated during prior migration in the storage reservoir making our calculations applicable. This could also depend on leakage rates. Those have been constrained for natural CO<sub>2</sub> analogues [43], but it is unclear how that translates to other settings. Leakage for such fields showed that, for example, the elevated He concentrations are maintained up until the surface [44].

Our calculations assume full equilibration of the injected CO<sub>2</sub> with formation water. In [13], we argued that equilibrium is likely to be reached, considering that at the front

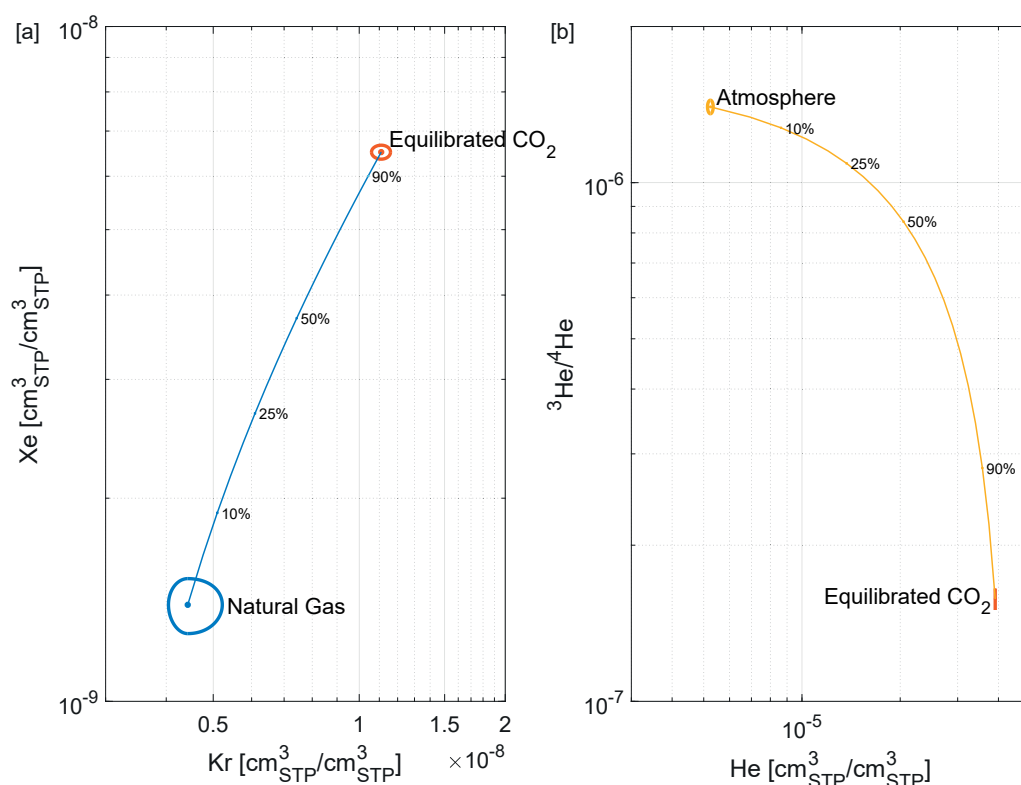
of a moving CO<sub>2</sub>-plume, the concentration gradients between the two phases, formation water, and CO<sub>2</sub> are high. For a dedicated storage case, such a behavior was, for example, observed at Aquistore, where the injected CO<sub>2</sub> had adopted a radiogenic signature one year after injection [11]. In contrast, the formation water of a system that is continuously flushed may become depleted in the noble gases over time, leading to domination of the depleted, original signature of the captured CO<sub>2</sub>. Such a behavior was observed for the specific case of the Cranfield EOR field [16]. Although, in that case, the presence of a hydrocarbon phase meant low residual water saturation and a limited volume of water in contact with the CO<sub>2</sub> phase, leading to more rapid noble gas stripping than would be observed for CO<sub>2</sub> storage in saline aquifers.

In the phase-partitioning and subsequent mixing calculations, the dissolution of CO<sub>2</sub> into the brine over time is not taken into account. This effect would tend to increase the residual noble gas concentrations and reduce the gas water volume ratio,  $V_g/V_{H_2O}$ . Our calculations do not evaluate the migration of a dissolved CO<sub>2</sub> phase. It is known (from natural analogues) that ex-solution of dissolved CO<sub>2</sub> tends to lead to quantitative partitioning of the dissolved noble gas load into the CO<sub>2</sub> phase and, thus, the reservoir signature is likely to be inherited [44]. However, the complexities of multistage dissolution–ex-solution have not been assessed in this study, and further investigation of the preservation of the noble gas signature in such systems is merited.

#### 4.2.3. Mixing Calculations

Mixing calculations of end-members will not allow the complete exclusion of a minor contribution of one end-member to a mixture, due to analytical uncertainty typically being an unsystematic error in the sample measurement [45]. Further, noble gases are found in every natural system and exhibit significant natural concentration variability, thereby introducing uncertainty in end-member calculations. The use of element or isotope ratios helps to reduce this uncertainty in mixing calculations because of the covariance of element or isotope concentrations, which removes dilution or concentration effects that otherwise create variability in absolute element concentrations. Further, the calculations become more constrained the more accurately the end-member compositions are known from baseline characterization of the storage system or via measurements of the captured and injected CO<sub>2</sub>. For example, above hydrocarbon systems, methane releases may imprint fluids in seafloor sediments with a radiogenic signature, reducing the distinctiveness of leaking CO<sub>2</sub> into the surrounding environment (Figure 1). Further, the gas hydrates composition is only known for the element and not the isotopic ratios, resulting in an incomplete description of one possible end-member.

Despite these uncertainties, noble gas signatures will deliver strong evidence when analyzing the fluids of a potential leak, as our calculations have shown. In Figure 2, only one element was used. By combining the analysis of a number of isotopes or ratios, the vector of the mixing line representing possible solutions to the mixing calculation increases; thereby, measurement errors become less influential. This is exemplified for a mixing with natural gas, where using both Kr and Xe increases differentiability (Figure 3a). Meanwhile, for atmosphere, the inclusion of the <sup>3</sup>He/<sup>4</sup>He ratio has the same effect. Besides, noble gases such as this could include additional geochemical constraints, such as the stable isotopic composition of the CO<sub>2</sub>. For example, injected CO<sub>2</sub> with an atmospheric <sup>13</sup>C isotope signature provides an additional distinct parameter with which to discriminate the CO<sub>2</sub> from natural gas [6].



**Figure 3.** Increasing the dimension of included isotopes/ratios increases differentiability. (a) Mixing with natural gas using both Kr and Xe. (b) Mixing with the atmosphere including  $^3\text{He}/^4\text{He}$ . The mean concentration is surrounded by the respective error ellipses.

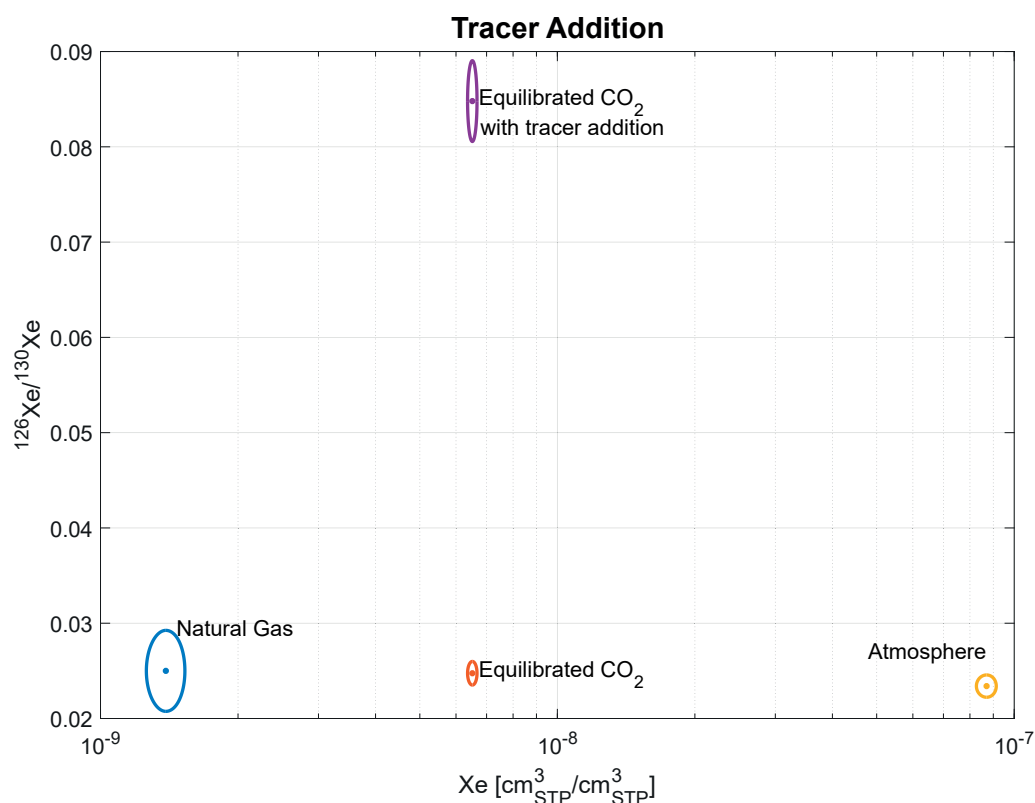
A further approach to reduce uncertainty introduced by natural variability is the addition of artificial tracers, e.g.,  $\text{SF}_6$  or PFCs. Since these are not present in the natural environment, uncertainties are reduced to the analytical uncertainty alone. Partly, however, these tracers have other disadvantages, such as toxicity or functionality as a greenhouse gas [18]. For details and examples, the reader may be referred to [15,18], where the addition of artificial trace gases is also analyzed from a cost perspective.

#### 4.3. Tracer Addition

Tracer addition could help to manage the limitations of the calculation, as described in the previous Section 4.2, i.e., increase the altering of the injected CO<sub>2</sub> signature of a mixture against the natural variability and the analytical uncertainty. The additional distinction through the addition is depicted for Xe and  $^{126}\text{Xe}/^{130}\text{Xe}$  in Figure 4.

The necessary concentrations to be added into the injection stream are lowest for  $^3\text{He}$  and  $^{124,126}\text{Xe}$  isotopes with concentrations of  $\sim 1\text{E}-10 \text{ cm}^3_{\text{STP}}/\text{cm}^3_{\text{STP}}$  or of 50–100 l/MtCO<sub>2</sub>. These He and Xe isotopes are among the most expensive in terms of cost per liter, at 1000–10,000 \$US/l (Table 4). Despite this, due to the small amounts required, these would be the cheapest tracers to add with a cost of  $\sim 0.7 \text{ $US}/\text{tCO}_2$  (Table 4).

Xe tracer addition appears to be the most suitable noble gas tracer in CO<sub>2</sub> storage, as both lab and field experiments suggest that Xe could even have an early warning function, in contrast to He [46,47]. This is due to the molecule size, i.e., allowing He to enter smaller, dead-end pores and thereby getting retarded. Adding  $^3\text{He}$  would also shift the  $^3\text{He}/^4\text{He}$  ratio towards atmospheric values, thereby interfering with the distinction to atmospheric signatures. Further,  $^3\text{He}$  has seen a price increase and supply shortage in the last decades [48] that may make its application unfeasible within a few decades. In contrast, availability of Xe isotopes is estimated to be sufficient [15].



**Figure 4.** The impact of tracer addition: The signatures of natural gas, equilibrated CO<sub>2</sub>, and atmosphere in comparison to the equilibrated CO<sub>2</sub> with tracer addition. The mean concentration is surrounded by the respective error ellipses.

The cheapest tracer addition would cost  $\sim 0.7$  \$US/tCO<sub>2</sub>, given our assumptions. In comparison to the cost of noble gas tracer addition derived with the method in [18], i.e., “10 times the detectable perturbation above background levels”, the cost estimates derived in our study are typically higher (Table 4). Even though the same isotopes are assigned the lowest cost in the derivation of [18], the cost presented here is several orders of magnitude more expensive, e.g., for <sup>126</sup>Xe 0.00014 \$US/tCO<sub>2</sub> after the method in [18] vs. 0.76 \$US/tCO<sub>2</sub> for the derivation presented here. Our results are also higher, but more in line with calculations for detection in soil gas made in [15], which resulted in a cost of  $\sim 0.1$  \$US/tCO<sub>2</sub> for both <sup>3</sup>He and <sup>136</sup>Xe.

Our criterion for distinctiveness of CO<sub>2</sub> in leakage detection schemes and considering the phase partitioning estimates leads to higher volumes of tracers needed and increased costs compared to previous studies [15,18]. However, defining when a signature is sufficiently distinct is, to a certain degree, a subjective choice. It appears that this will have to be defined by decision makers, i.e., how soon and how certain one wants to know a leakage/contamination in a trade-off between cost and risk.

In comparison to total operational costs of a CCS project,  $\sim 0.7$  \$US/tCO<sub>2</sub> is a low cost, for example, compared to a CO<sub>2</sub> capture cost of 15–120 \$US/tCO<sub>2</sub> [49]. However, considering that the current cost of the whole monitoring scheme of running sites is in the order of 1–4 \$US/a [1], the added cost would be a significant contribution to the total monitoring cost, especially considering the generally low leakage likelihood [50]. Further, on the one hand the estimated cost does not yet include sampling, analysis, and evaluation costs, on the other hand there may be a price reduction through bulk orders of the respective tracer gas.

#### 4.4. Technical Aspects of Tracer Addition

The addition of a noble gas tracer into a CO<sub>2</sub> injection stream represents an impurity, which potentially changes the thermodynamic properties of the CO<sub>2</sub>. Even though indi-

vidual for each CO<sub>2</sub>-tracer mixture, depending on the type and amount of an impurity, typically, the critical pressure is increased [51]. This implies changes of the transport properties and could affect transportation and injection setup, and is thus likely to add costs. Impurities also tend to decrease the viscosity of the fluid mixture [51], reducing migration properties of the CO<sub>2</sub> in the reservoir. Therefore, it seems desirable to have the lowest concentrations of the added tracer as possible. For the trace isotopes we derive as most economical, i.e., elemental He and Ar being excluded, the added impurity is very low (below 1E-06 vol%) compared to those typically found after the CO<sub>2</sub> capture process, such as N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>S, and H<sub>2</sub>O which can collectively make up 1–5 vol%) [52].

On another technical note, achieving continuous tracer concentrations in a gas stream as low as 1E-11–1E-10 cm<sup>3</sup><sub>STP</sub>/cm<sup>3</sup><sub>STP</sub> is not trivial. Nimz and Hudson [15] outline how a side-track with flow regulation and an additional compressor could be used. It is also suggested that the low volumes of the gas necessary, e.g., tenths of liter per year, could better be applied through prior mixture with CO<sub>2</sub> as the carrier gas, i.e., stepwise dilution [15]. It might also be considered to have pulsed injection patterns and assume effective distribution after injection.

#### 4.5. Noble Gases in Monitoring Schemes

In case of an observed or suspected CO<sub>2</sub> anomaly or leakage, noble gases are very likely to give an indication of the CO<sub>2</sub> source due to the distinct signatures in the environment. Therefore, noble gases' main application will—also offshore—lie in leakage attribution as it has in the past, e.g., [14].

In contrast, high-frequency monitoring of a storage site for leakage detection, does seem less attractive given that noble gas analysis for high sensitivity, precision, and accuracy—i.e., full isotopic analysis including the least abundant isotopes—currently has to be conducted using a lab-based multicollector mass spectrometers with a cost of up to several thousand \$US per sample. Further, collecting and transporting a sample to the lab does introduce a significant time lag between sampling and interpreting results.

However, in recent years, in situ, continuous, and remotely controllable noble gas analysers have been developed [53,54]. Currently these techniques cannot deliver full isotopic resolution, typically covering the most abundant elements of a noble gas, e.g., <sup>4</sup>He, but not <sup>3</sup>He. Further, the limit of quantification is usually in the ppm range. Still, with on-site measurements, not only leakage attribution but also leakage detection may become possible. Especially, the elevated concentrations of He (see Table 3) could be targeted with a mobile mass spectrometer when sampling offshore seabed fluid releases, as demonstrated in the vicinity of black smokers [53]. Both water and gas analysis could be conducted on board a ship to scan if elevated He concentrations indicate leaking CO<sub>2</sub> from a deep CO<sub>2</sub> source with a radiogenic signature. Simultaneous measurement of O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>, which the instrument is capable of, add valuable information.

In contrast to the previous case, the application of these technologies for the monitoring of the production stream at an operating gas field is limited. Considering our results, e.g., for the mixture of CO<sub>2</sub> and natural gas, where Xe is the most distinctive gas, the portable analysis systems do currently not deliver sufficient sensitivity for detection of Xe concentrations of 1E-09 cm<sup>3</sup><sub>STP</sub>/cm<sup>3</sup><sub>STP</sub>, even with tracer addition (see Table 3). Further advances of these technologies may allow for wider applicability and for continuous, remote leakage detection.

## 5. Conclusions

The partitioning of the formation water noble gas signature into injected CO<sub>2</sub> is destined to allow the differentiation from natural geological fluids or gases due to the specific fractionation through the phase partitioning in a CO<sub>2</sub>-H<sub>2</sub>O-system. Meanwhile, there are uncertainties attached to the distinction towards natural gas, i.e., unknown solubilities in a CH<sub>4</sub>-H<sub>2</sub>O-system, the difference between the adopted radiogenic signature and that of shallow signatures is very pronounced.



The presented approach also allows us to evaluate the active addition of a noble gas tracer to the injection stream with the goal of maintaining a significantly different noble gas signature after the equilibration. Xe isotopes are the most relevant choice for noble gas tracer addition, since they have the lowest concentrations in the background (see Table 1) and do not impact the main features of the radiogenic signature, in contrast to He. Such an addition will increase identifiability but adds significant cost to a monitoring scheme of a storage project.

Further, baseline characterization is fundamental, and even though we use relevant analogues in this study, each storage site and CO<sub>2</sub> capture plant has to be expected to be different. For the inherent recognition through Xe, specific fractionation patterns in captured CO<sub>2</sub>, such as elevated Kr and Xe at oxyfuel plants, could significantly increase detectability. Further, formation water concentrations are only indirectly derived.

Considering that CCS is currently only feasible with government subsidies, adding cost to CCS projects endangers its large-scale application [3]. Therefore, implementation of a noble gas tracer addition and other MMV methods will, on the one hand, depend on the legal framework regarding long-term liability of safe containment, and on the other hand, on widespread and meaningful implementation of carbon pricing options, such as carbon taxes or a carbon trading system. Further, (i) with the involved techniques maturing over the past and coming decades, uncertainties attached to such advanced green investments should reduce and thereby improve the green finance framework [55]; (ii) and increased MMV expenditures could increase the environmental reputation of the involved entities [55].

The planned, continuous MMV program in the Norwegian storage project 'Longship' currently does not include noble gases [27]. We believe that noble gas sampling should be considered during routine environmental surveys and should definitely be the content of 'triggered' environmental monitoring surveys. The content of such a triggered environmental monitoring survey has yet to be defined.

This work is another step towards upscaling and realizing the utilization of noble gas tracers, quantitatively and qualitatively describing how noble gases can be applied, which behavior is to be expected, and how they may be useful in deploying CCS. Implementation in case-specific leakage models, including secondary processes such as dissolution and mineralization of CO<sub>2</sub> combined with advances in defining solubilities of noble gases in the relevant systems and further developments in field-applicable measurement devices, will constrain our findings further and allow for wider application of noble gases in monitoring schemes for CO<sub>2</sub> storage sites, enhancing detectability and source attribution.

**Author Contributions:** Conceptualization, U.W.W., N.K. and A.S.; methodology, U.W.W., N.K. and A.S.; software, U.W.W. and N.K.; formal analysis, U.W.W.; investigation, U.W.W.; writing—original draft preparation, U.W.W.; writing—review and editing, U.W.W., N.K. and A.S.; visualization, U.W.W., N.K. and A.S.; supervision, A.S.; project administration, U.W.W. and A.S.; funding acquisition, A.S. All authors have read and agreed to the published version of the manuscript.

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Paper IV

# **Geochemical Evidence for Cross-Fault CO<sub>2</sub> Migration in a Caprock**

**U. W. Weber, A. P. Rinaldi, C. Roques, A. Zappone, S. Bernasconi, M. Jaggi, Q. Wenning, S. Schefer, M. Brennwald, R. Kipfer**

Unsubmitted Manuscript, 2021



# **Appendices**





# Appendix A

## Conference Papers

The conference papers collected here represent minor contributions that lead the way to the main papers. This involves two Greenhouse Gas Control Technologies Conference (GHGT) papers and one Trondheim Carbon Capture & Storage Conference (TCCS) paper.

The GHGT-14 paper shows the results of a feasibility study that set the foundation for Paper II. The GHGT-15 paper is, on the one hand, an important contribution in itself by characterizing an additional CO<sub>2</sub> capture plant and increasing the range of signatures found in captured CO<sub>2</sub> and, on the other hand, a development of the phase partitioning calculations started in Paper II. In the contribution to TCCS-11 a baseline dataset for a North Sea storage site is collected and a specific example of tracer addition is calculated. The two latter papers therefore form the basis for Paper III.

### **A.1 In-Line Variations of Noble Gas Concentrations During CO<sub>2</sub> Capture Operations by Means of a Portable Mass Spectrometer**

**Authors** A. Sundal, U. W. Weber, M. S. Brennwald, P. Ringrose, N. Flø, K. Johnsen, L. Faramarzi, P. Aagaard, R. Kipfer

**Conference** 14th Greenhouse Gas Control Technologies Conference Melbourne, 21-26 October 2018 (GHGT-14)

**DOI** 10.2139/ssrn.3366166

**Summary** This conference contribution presents the results of a feasibility study that laid the foundation for the ICO<sub>2</sub>P project. Here, we conducted a five day sampling campaign at the Technology Centre Mongstad in 2018.

The goals were mostly to address practical issues for setting up the portable mass spectrometer on-site and sampling the gas for subsequent analysis in the laboratory. The installation was achieved easily within an hour and a secure set-up for the gas flows was found in cooperation with the local staff. The time series also resulted in two observed changes in Ar and He concentrations, respectively. Single samples were taken in gas sampling bags. It turned out that the sampling bags were not tight over the long run and air-like composition was measured a couple of months later in the ETH laboratory. This is generally a valuable finding, and one should only use gas bags for sampling when they will be analysed right away. The measurements with the portable mass spectrometer

## A. Conference Papers

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could, therefore, not be verified. In conclusion, the results were motivating further sampling campaigns, which are presented in Paper II.



14th International Conference on Greenhouse Gas Control Technologies, GHGT-14

21<sup>st</sup> -25<sup>th</sup> October 2018, Melbourne, Australia

## Monitoring real time, in-line variations of noble gas concentrations during CO<sub>2</sub> capture operations by means of a portable mass spectrometer

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### Abstract

In the ICO<sub>2</sub>P-project the overall aim is to develop an innovative and cost-effective monitoring scheme for CO<sub>2</sub> capture and storage operations, implementing new methods for in situ noble gas measurements. The first step is to establish a basis for fluid source identification by recording temporal variance of noble gas composition in CO<sub>2</sub> product. Studies of noble gases related to CCS typically include few, single point samples. In ICO<sub>2</sub>P, a portable mass spectrometer (i.e. miniRUEDI) is utilized to directly measure real time variability of the noble gas content in CO<sub>2</sub> gas streams at operating CCS facilities. The first study was performed at the Technology Centre Mongstad (TCM) in Norway, a large-scale test facility for post-combustion CO<sub>2</sub> capture operations. During an open scientific test campaign for amine-based capture (TSA-MEA), noble gases (He, Ar, Kr) as well as CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> concentrations in the CO<sub>2</sub> product stream were recorded every 10 to 15 minutes during a 5-day period. He concentrations (<0.001ppm) were depleted post-capture and too low for temporal variation measurements in the CO<sub>2</sub> product line. Ar concentrations (0.15 – 0.65 ppm) were significantly higher and temporal variation was successfully recorded in the CO<sub>2</sub> product line. Ar was found to be sensitive to capture operations, e.g. CO<sub>2</sub> recycling ratio. This new approach will provide knowledge of the uniqueness and variability of inherent noble gas fingerprints and depletion/absorption during CCS operations and provide grounds for comparison between fluid origins needed in leakage detection schemes at CO<sub>2</sub> storage sites.

*Keywords:* CO<sub>2</sub> storage; CO<sub>2</sub> capture; CCS; noble gases; monitoring;

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## 1. Introduction

During a recent feasibility study [1], to assess the potential for real-time, semi-continuous noble gas monitoring, data were collected from CO<sub>2</sub> capture operations at the Technology Centre Mongstad (TCM) in Norway (Fig. 1), using a novel method for quantitative gas composition measurement. The overall aim has been to contribute towards developing innovative and cost-effective monitoring schemes for CO<sub>2</sub> capture and storage operations, work that is now part of an ongoing research project - the ICO<sub>2</sub>P-2 project [1] during 2018-2021.

By recording temporal variance of noble gas composition in CO<sub>2</sub> capture products, the inherent geochemical fingerprint can be evaluated with respect to the potential for source identification at prospective storage sites (i.e. differentiation of sources at CO<sub>2</sub> seepage sites or natural variations in marine and terrestrial environments). Studies so far typically include only a few, single point samples, and there is a clear need for more background data on gas compositions and better sampling strategies to ensure safe storage and reliable leakage detection. The miniRuedi [2] portable mass spectrometer has the capacity to measure low concentrations (i.e. partial pressures) of He, Ar and Kr, as well as CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub> and other relevant chemical substances with high accuracy at sample intervals of < 15 minutes. This technology proved suitable for monitoring fluctuations in some components of the CO<sub>2</sub>-product composition, as tested during an open scientific test campaign for post-combustion capture processes; amine-based temperature swing absorption (TSA), at TCM in summer 2017.

This data set, and further work, will provide important knowledge on absolute variability in CO<sub>2</sub> product from complex and mixed sources. During capture operations and before storage of CO<sub>2</sub> can commence, there is a need to document variability, and to evaluate the inherent compositional signature (and the potential need for adding tracers). This approach will allow for source-specific identification of fluids; differentiating injected (anthropogenic) CO<sub>2</sub> from natural (methanogenic / biogenic) CO<sub>2</sub> rich gases at potential leakage points.



Fig. 1. Technology Centre Mongstad (TCM), Norway [Photo © Equinor] DA amine plant with CHP flue gas inlet from the front, and the high absorber tower in the middle. “Captured” CO<sub>2</sub> product outlet and sample point towards the right.

## 2. Noble gases as tracers in CCS (and EOR)

Reliable monitoring is a prerequisite for safe, long-term storage and public acceptance of CCS. Terrestrial noble gases (i.e. He, Ne, Ar, Kr, Xe) appear to be suitable natural tracers for monitoring and understanding CO<sub>2</sub>-rich gas systems [3]. They are chemically inert and non-degradable. And in contrast to several commonly applied chemical tracers (e.g. PerFluoroCarbons), inherent noble gases are not harmful to the environment and bring no additional cost. The concept of using noble gases for monitoring CO<sub>2</sub> projects has been demonstrated at small-scale onshore facilities, and noble gas data proved to be crucial evidence to rule out an alleged leakage incident at the Weyburn project [4].

However, there are still knowledge gaps: studies so far typically include only a few, single-point samples, and there is a clear need for better data on gas compositions and variability.

To understand large-scale reservoir dynamics and fluid mixing at CO<sub>2</sub> injection sites and along possible leakage paths, experience from research related to multi-phase hydrocarbon systems have to be used and adapted to the scientific case of CCS. Formation water in deep, saline aquifers will have a unique noble gas signature based on a blend of an atmospheric component (stable contents of <sup>20</sup>Ne, <sup>36</sup>Ar, <sup>84</sup>Kr), a deep mantle component (mostly supplying <sup>3</sup>He) and a crustal radiogenic component (production of <sup>4</sup>He, <sup>21</sup>Ne, <sup>40</sup>Ar). The signature is a function of time and dependent on the in-situ lithology [5]. Crustal <sup>4</sup>He is supplied from radiogenic decay of U and Th in minerals, and <sup>40</sup>Ar is produced by radioactive decay of <sup>40</sup>K. The mixing ratios of meteoric, mantle and crustal components may yield information about residence times and fluid mixing. E.g., it was found that seepage of methane causes depletion of <sup>20</sup>Ne and <sup>36</sup>Ar relative to <sup>4</sup>He by partitioning, as the heavier noble gas species are more soluble in methane than in water [5]. Exchange between groundwater and oil phase may also be detected as increased <sup>20</sup>Ne and <sup>36</sup>Ar abundance in oil, as described for the Magnus Field in the British North Sea [6]. Injected CO<sub>2</sub>-rich fluid will also interact with formation water and/or hydrocarbon phases present in a storage reservoir. A recent tracer test at the Cranfield enhanced oil recovery (EOR) field in the US, adding Kr and Xe, showed noble gases to be stripped from formation water and into the CO<sub>2</sub> phase [7]. Mapping of the background noble gas abundance before injection is of utmost importance to characterize the natural gas composition and spatial distributions prior to CO<sub>2</sub> injection. This will improve the understanding of CO<sub>2</sub> trapping mechanisms and oil/water/gas partitioning in reservoirs, and form the grounds for comparison needed in leakage detection schemes.

### 2.1. Compositional variability in captured CO<sub>2</sub>

Norway is currently at the forefront in developing CCS, along with Canada, Australia, USA and China. With two active storage sites and a national plan to establish another, larger-scale offshore storage site at Smeaheia, there is an imminent need to prepare reliable, cost-effective and long-term monitoring programs. Noble gas finger-printing can provide an applicable solution, but there is a significant knowledge gap concerning the inherent signature of CO<sub>2</sub> from various capture processes.

At the operative Sleipner and Snøhvit sites, inherent CO<sub>2</sub> from fossil sources (natural gas reservoirs) is captured (as part of the gas processing) and re-injected into a storage formation (saline aquifer). Such single-source storage schemes are expected to display the least degree of temporal variation in the noble gas compositions of injected gas. The noble gas signature of a given natural gas accumulation is related to long-term, slow accumulation rates of e.g. <sup>3</sup>He, <sup>4</sup>He, <sup>21</sup>Ne, <sup>40</sup>Ar in a given geological setting. Lateral or vertical compositional gradients in reservoirs related to the lithology and contact time with fluids in traps and along migration paths, may be documented as compositional changes during production. However, these changes are expectedly subtle, compared to complex mixed-source and post-combustion schemes. At the Technology Centre Mongstad (TCM) the source is mixed, and natural gas from several reservoirs are combusted before CO<sub>2</sub>-rich flue-gas enters the capture facility. CO<sub>2</sub> is captured from a combination of flue gases; (1) from a combined cycle gas turbine (CCGT) based heat and power plant (CHP) or (2) the residual fluid catalytic cracker (RFCC) at the Equinor refinery at Mongstad. At the CHP plant large quantities of gases from different fossil sources are combined, but after initial mixing and combustion, the signature of the flue gases are expected to become relatively homogenous within a few days. Then, with addition of residual refinery gas, the compositional variability is expected to increase. Further, the combustion process will add an atmospheric component.

Depletion of the radiogenic/nucleogenic components of reservoir derived noble gases occurs during combustion and capture [8]. In the product line recirculation rates, addition of different solutes with given solubilities for the gases and their isotopes under varying pressure and temperature conditions will affect noble gas contents. In this study, we attempt to document temporal changes, and the next step is to interpret and decipher the relative effects of capture processes on noble gas fingerprinting. Additionally, documenting variation in the fossil gas feed is highly relevant in evaluating the traceability of mixed-source gas in future storage schemes, involving captured CO<sub>2</sub> also from other industries (e.g. cement, ammonia, waste incineration, biogas). E.g. the presented storage scheme for Smeaheia involves storage of CO<sub>2</sub> from mixed sources, after post-combustion capture.

### 3. Methodology

#### 3.1. Capture processes at TCM

The Technology Centre Mongstad (TCM) is a large-scale test facility for CO<sub>2</sub> capture operations. This study was conducted in July 2017 during an open scientific test campaign for post-combustion capture processes, using amine-based temperature swing absorption (TSA) [e.g. 9, 10, 11]. Monoethanolamine (MEA) is used as solvent for CO<sub>2</sub>. The combined cycle gas turbine and power plant is run with reservoir gas from different fields in the North Sea mixed with a fraction (up to 50 %) of residual gases from the nearby refinery. Flue gas is fed into the TCM plant, cooled, run through the absorber, before CO<sub>2</sub> is stripped off by heating the solvent and vented to a safe location in a dedicated vent stack (Fig. 2). During the test period, the capture plant was run with flue gas from the CHP plant, with a CO<sub>2</sub> concentration of approximately 4 vol%. In addition, recycling (i.e. return of CO<sub>2</sub> product back to feed gas upstream absorber) was performed, increasing the CO<sub>2</sub> content to mimic concentrations similar to coal combustion capture (Fig. 2).

#### 3.2. Portable mass spectrometer

The adapted mass spectrometric technology for analyzing extremely low concentrations and the isotopic fractionations of He, Ne, Kr, Xe, Ar in water and gas is available only in few laboratories worldwide, with the research laboratory at Eawag/ETH (Zürich) being one of the pioneers in this field.

The miniRuedi (Fig. 3) allows for semi-continuous gas analysis (i.e. partial pressures), and may be used to measure noble gas concentrations. It consists mainly of two vacuum pumps (DP, TP) and a quadrupole mass spectrometer (QMS) with two detectors (Faraday and Multiplier) with different sensitivities. In contrast to fixed laboratory units, no purification by e.g. cryogenics is carried out, which reduces the detection limits, but allows for on-site measurements and smaller instrument units [2]. The instrument has several inlet ports such that a standard gas for calibration and multiple samples can be measured subsequently and automatically without changing the setup. The consumption rate of sample gas is negligible low compared to passing gas streams.

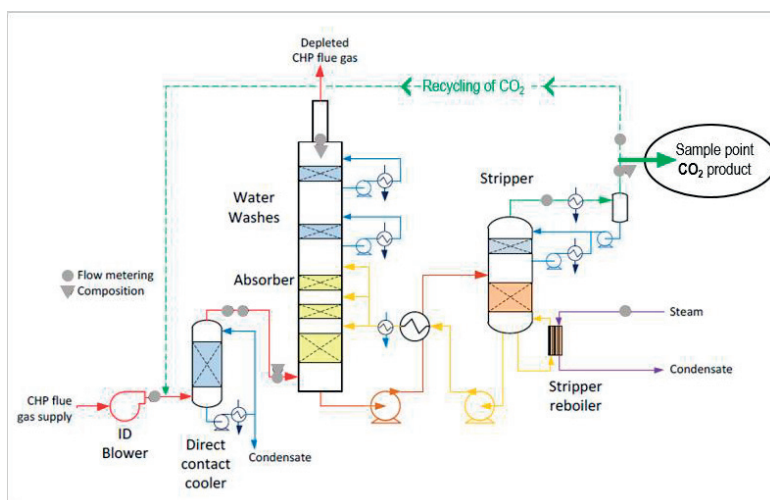


Fig. 2. Post-Combustion CO<sub>2</sub> capture at the Technology Centre Mongstad during TSA-MEA test campaigns. A mobile mass spectrometer was connected to the CO<sub>2</sub> product line. Modified from Thimsen et al. [9]

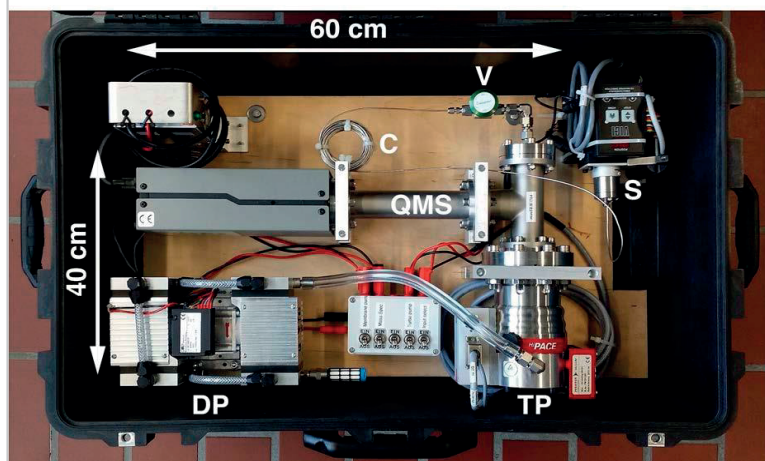
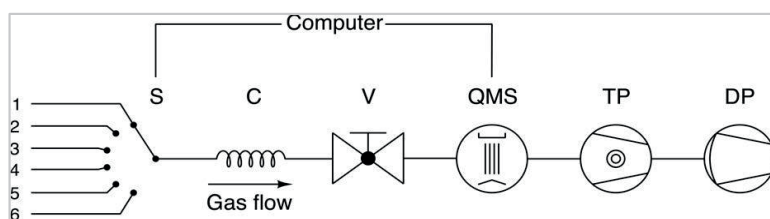


Fig. 3. The miniRuedi portable mass spectrometer (figure from Brennwald et al. [2]) set up with 6-port inlet selector valve (S), capillary (C), inlet valve (V), quadrupole mass spectrometer (QMS), turbomolecular pump (TP), and diaphragm pump (DP).

### 3.3. Sample set-up

A miniRuedi [2] mass spectrometer was connected to the outgoing CO<sub>2</sub> product line, downstream the overhead condenser of the CO<sub>2</sub> stripper (Fig. 2). This stream is water-saturated, and the slip-stream to the instrument was passed through a dryer to avoid the risk of condensation in the instrument. A pressure regulator was mounted between the sample point and the membrane inlet to decrease the inlet pressure to atmospheric pressure. This inlet pressures were fairly constant and recorded with a pressure sensor. The instrument was mounted in less than 1 hour, and ran continuously during a 5-day test period. The analytical sequence was set to repeating cycles of one air-standard analysis block (calibration), followed by three CO<sub>2</sub> output stream sample analysis blocks. An ambient air sample analysis block was added intermittently to remove residual CO<sub>2</sub> from the ion source. The analysis blocks lasted between 10 and 15 minutes depending on the number of components measured. During the test He, H<sub>2</sub>O, Ne, N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub> and Kr were measured. In this way, a unique, semi-continuous data series of gas content was collected and suitable measurement routines were established. Single samples were gathered for lab analysis of noble gas isotopes.

## 4. Results

The instrument ran steadily throughout the sampling period. However, as this was a feasibility study, parameters such as air-calibration and sampling intervals as well as the selection of analyzed components were tweaked and tested underway. Absolute concentrations of CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> were compared with measurements performed by TCM (in-line gas-chromatography). Low concentrations of noble gases throughout the measuring campaign confirm depletion during capture. Kr and Ne were excluded after initial sampling tests, as their partial pressures were below the detection limit. He was too low (< 0.001 ppm) throughout for proper quantification with the miniRuedi, as peak variation could not be deciphered from background. This was confirmed in new, preliminary data analysed after the GHGT poster presentation, and thus He plots are excluded from this final summary. Further studies of single samples and continuous measurement of pre-capture variation (source inlet) are ongoing.

Ar (150 – 650 ppm) contents were significantly higher compared to He, Kr, Ne, and was measured throughout the 5-day sampling period (Fig. 4). Some significant changes were observed (i.e. sudden increase/decrease). The

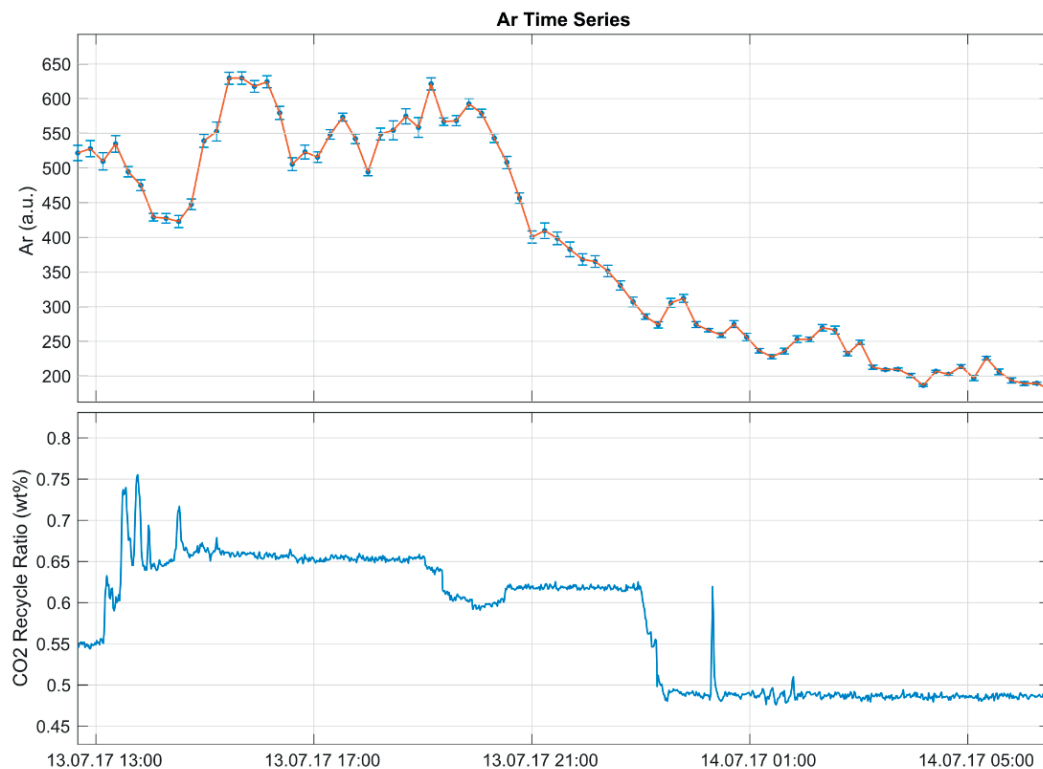


Fig. 4. Measured Ar concentrations (ppm) during the test period 10.07. – 15.07.2017 (upper) displaying co-variance with CO<sub>2</sub> recycle ratio (wt %) at the TCM plant (lower).

analytical error at sampling intervals of 10 - 15 minutes was acceptable, but the standard gas (air) used for calibration was found to be sub-optimal. Ar concentrations appear to be sensitive to changes in the recycle ratio and the capture process (Figs. 4, 5). Preliminary results from single samples confirm that He content is lower in the refinery gas compared to in the natural gas source, and concentrations are expected to vary according to relative contributions from natural gas versus refinery gas (Fig. 6). An observed decline in measured Ar concentrations coincided with reduction of CO<sub>2</sub> recycling in the line, a scheduled process change (Fig. 4).

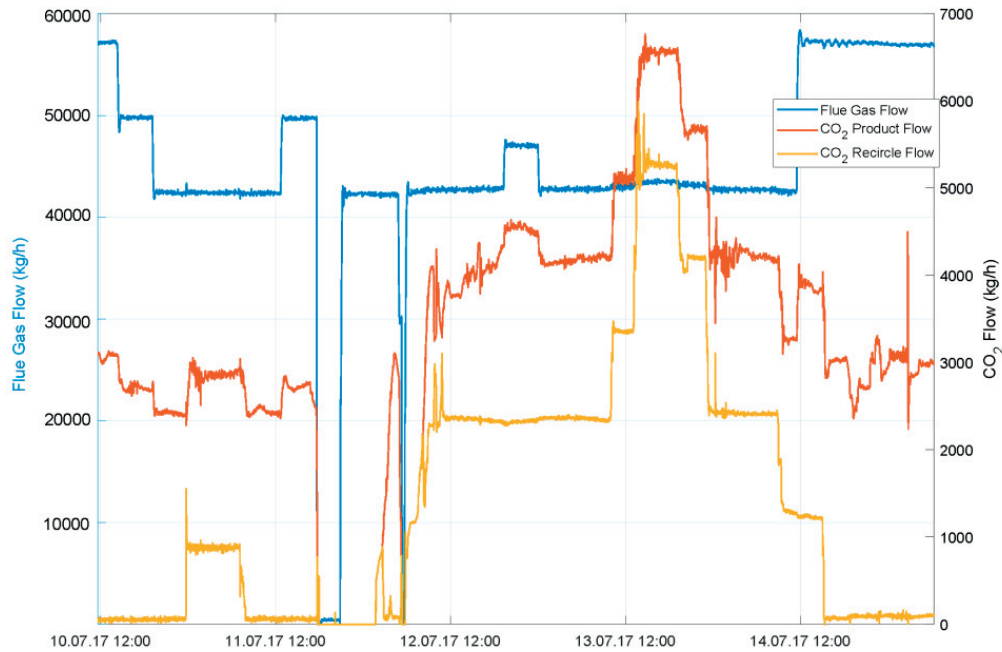


Fig. 5. Gas flows (kg/h); flue gas, CO<sub>2</sub> product and recycled CO<sub>2</sub>.

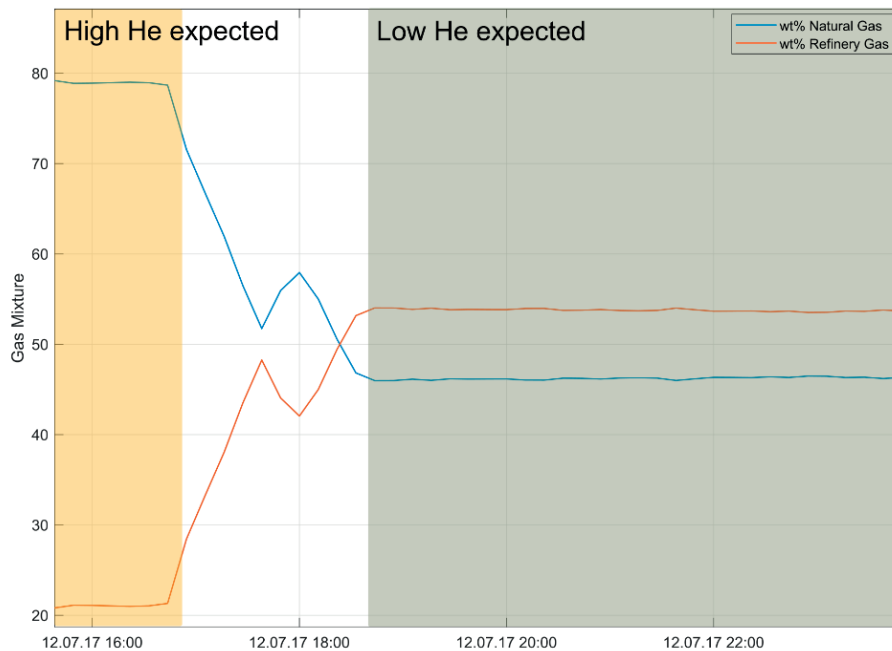


Fig. 6. Change in flue gas composition (wt % refinery gas vs. natural, detail from Fig. 5). Single samples indicate lower He concentrations in RFCC flue gas, such that concentration changes are expected for different mixing ratios.



## 5. Discussion

The test was successful in that the miniRuedi instrument ran continuously and variation in Ar concentrations were observed and documented. Up to 50 % change in relative concentrations of Ar was observed in the course of 5 days. This shows that there is noble gas variability, and that continuous monitoring is useful to ensure representative sampling in evaluation of inherent fingerprints and traceability. Preliminary single sample results show that concentrations are detectable with our technique before absorption (capture). During gas combustion and in the RFCC process, contamination with air occurs.

Assuming that tests during the capture processing (e.g. recycling) in a regularly working plant are not occurring, variations due to the capture process are expected to be minor. Thus noble gas variation related to source rather than process changes should be measured/detectable at the inlet. This is evaluated in ongoing studies.

The approach of in-line monitoring with a miniRuedi instrument is straightforward. However, optimization is necessary in order to reduce analytical uncertainty. Sample intervals of ~ 10 minutes were found suitable with respect to signal reading time and peak heights, and relative to sample resolution (gradual compositional changes). A customized calibration gas more similar to the CO<sub>2</sub>-product should be used in future tests for improved accuracy. Absolute variability in Ar concentrations was registered, and may be used to guide sampling for further chemical analysis and noble gas isotopic signature, ensuring a representative data set of single samples.

TCM is a test facility, and thus the CO<sub>2</sub> product is not stored. There are, however, plans to establish a full value CCS chain in Norway, including storage of CO<sub>2</sub> captured post-combustion [12]. Storage of CO<sub>2</sub> from multiple sources (e.g. fossil fuels, cement, waste incineration) and different capture operations are challenging. Semi-continuous noble gas analysis may allow for pre-injection gas fingerprinting. With regards to detectability at potential leakage sites and separation of different anthropogenic type sources in reservoirs, however, some additional tracer gas may have to be added. At single-source sites (e.g. Snøhvit, Utsira), inherent fingerprints may suffice for source identification. For evaluation of source variability and the effect of the capture process on noble gas signatures, both the flue gas supply (inlet) and CO<sub>2</sub> product (outlet) should be monitored simultaneously. Multiple capillary inlets to the miniRuedi instrument allows for semi-continuous monitoring of several sample points. Total variation estimates are useful to guide sampling for isotopic analysis.

Ar concentrations displayed significant variation. During the Ar decrease shown in Fig. 4 the recycling rate was adjusted. Even though this is a change that may not occur in a running large-scale capture site, the dramatic decrease emphasizes that there is a response in the noble gas assembly related to capture process changes. During the test period measurements indicate that noble gases were heavily depleted after capture. He concentrations are significantly lower than atmospheric concentrations (~ 0.00524 hPa). Alternative sampling techniques, e.g. [13], may be tested in further research for gases currently below detection limit (i.e. He, Ne, Kr). Monitoring in-line variation and correlating with isotopic fractions from previous samples will reduce the need for costly and time-consuming lab analysis.

## 6. Conclusions

The utilization of noble gases as added and/or natural tracers in the context of CO<sub>2</sub> storage monitoring is rather new. As CCS is being upscaled and put into practice, the need for combined and improved monitoring techniques is becoming evident. This feasibility study found that the miniRuedi [2] allows for frequent and accurate measurements of Ar abundance in captured CO<sub>2</sub> from a *post-combustion* like facility (TCM). Preliminary single sample analyses indicate detectability also for continuous measurements of variation in He in the flue gas supply (source) before absorption and depletion during *post-combustion* capture. At *pre-combustion* sites, however, contamination with air is expected to be significantly lower, and considering He concentrations (enriched during radiogenic production) measured in North Sea gas fields [6], monitoring temporal variations for He in the CO<sub>2</sub> product at *pre-combustion* capture sites is feasible. Documentation of variability in live gas streams and guided follow-up sampling for isotopic analysis in the lab will provide an important basis for consideration of noble gas fingerprints in monitoring schemes and leakage detection. This is a new approach that will provide knowledge of the uniqueness of noble gas fingerprints in the product stream from hydrocarbon production, CO<sub>2</sub> capture operations and in the injection line for CO<sub>2</sub> storage.

## Acknowledgements

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## **A.2 Noble Gases as Monitoring Tracers in CCS: A Case Study with CO<sub>2</sub> from the Waste-to-Energy Plant Klemetsrud, Norway**

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**Conference** 15th Greenhouse Gas Control Technologies Conference, 15-18 March 2021

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**Summary** This conference contribution presents the results of a sampling campaign at the Waste-to-Energy Plant Klemetsrud, Oslo, Norway. A complete dataset of the gas fluxes of a capture feasibility set-up was collected and analysed by the independent noble gas laboratory at Lancaster University, UK.

The goal was to characterize the noble gas content of the captured CO<sub>2</sub> of the waste incineration plant since it is targeted to be included in the Norwegian 'Longship' project. Further, the alteration of the CO<sub>2</sub> subsequent to injection was planned to be expanded.

The CO<sub>2</sub> showed, again, very different composition than what was previously measured at TCM and Snøhvit and other studies. In summary, the concentrations are the most depleted of any of the sites. This could be caused from the advanced degradation state the amine solvent was in during sampling.

The very low concentrations does only have a minor effect on the stripping of gas from the formation water. The phase partitioning is derived for a depth profile. Meanwhile there are significant changes, it does not impact the general conclusion of a radiogenic signature being overtaken by the injected CO<sub>2</sub>.





15th International Conference on Greenhouse Gas Control Technologies, GHGT-15

15<sup>th</sup> 18<sup>th</sup> March 2021 Abu Dhabi, UAE

## Noble Gases as Monitoring Tracers in CCS: A Case Study with CO<sub>2</sub> from the Waste-to-Energy Plant Klemetsrud, Norway

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### Abstract

To design monitoring schemes for CO<sub>2</sub> storage sites, the composition of the injected CO<sub>2</sub> needs to be characterized. Noble gases are one of the environmental tracers, which could be cost-effective since they are naturally inherent in the CO<sub>2</sub> and the storage reservoir fluids. The elemental, e.g. He/Ne, He/CO<sub>2</sub>, or isotopic, e.g. <sup>3</sup>He/<sup>4</sup>He ratios of a gas are potentially diagnostic fingerprints which can be used to discriminate gas sources in the environment, e.g. deep crustal versus shallow, biogenic gas.

The waste-to-energy (WtE) plant Klemetsrud, which generates 460000 tCO<sub>2</sub>/a, was investigated as a future source of captured CO<sub>2</sub> for storage in the up-coming large-scale CCS project 'Longship', in Norway, aimed to be operational by 2024. In 2019, a demonstration capture facility at the WtE plant was set up to establish the feasibility of future large-scale CO<sub>2</sub> capture. We sampled the main gas streams on-site and present the analysis of noble gases in (I) the exhaust of the waste incineration, i.e. the flue gas stream with high concentrations of CO<sub>2</sub>, (II) the capture outlet, i.e. the CO<sub>2</sub>-depleted gas stream and (III) the captured, concentrated CO<sub>2</sub> gas stream.

Noble gas concentrations are depleted in the captured CO<sub>2</sub> after the amine treatment by several orders of magnitude compared to the flue gas. Isotopic ratios are air-like. This behavior has been observed at other CO<sub>2</sub> capture plants. However, absolute concentrations of noble gases measured at Klemetsrud are significantly lower for all species, except He, which is within the range of previously measured concentrations.

Further, we apply phase partitioning calculations to investigate the application of inherent noble gas in CCS monitoring schemes. The low noble gas concentrations, and their associated elemental and isotopic ratios, would only be preserved when the injected CO<sub>2</sub> remains almost pure and does not mix or interact with fluids already present in the reservoir (e.g. native gas, formation water). Interaction of the CO<sub>2</sub> with the formation water will lead to noble gas stripping that overprints the highly depleted composition of the captured CO<sub>2</sub> with a noble gas elemental and isotopic ratios characteristic of deep crustal fluids. This characteristic signature, especially when coupled with the distinct major gas composition of leaked CO<sub>2</sub> (e.g. extreme CO<sub>2</sub>/CH<sub>4</sub> ratios) may form an effective tracer to discriminate a CO<sub>2</sub> leakage from other gas sources at the seabed (e.g. shallow biogenic, dissolved air or hydrate decomposition). To take advantage of this low cost tracer, baseline geochemical surveys should include inventories of the background dissolved noble gas load in the formation water of storage reservoirs, in other (hydrocarbon bearing) formations along the migration route and in existing seabed gas seeps overlying the storage site.

*Keywords: Norwegian full-scale CCS, Noble Gas Tracers, Monitoring, CO<sub>2</sub> Capture*

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## 1. Introduction

In the up-coming full-scale CCS project ‘Longship’ in Norway [1], CO<sub>2</sub> will be captured from onshore industrial sources in order to reduce Norway’s greenhouse gas emissions. Ships will transport the CO<sub>2</sub> to a gas terminal on the west coast of Norway, from where it will be transferred and injected via a sub-sea installation to be stored in the ‘Aurora’ reservoir prospect on the Norwegian continental shelf [1]. This full-scale CCS project is planned to be operational by 2024. The waste-to-energy (WtE) plant Klemetsrud may contribute up to 415000 tCO<sub>2</sub>/a in addition to CO<sub>2</sub> supplied from the approved capture facility at the Norcem cement plant.

Noble gas tracers (i.e. He, Ne, Ar, Kr, Xe) may be utilized in future measurement, monitoring and verification (MMV) schemes for the CO<sub>2</sub> storage site. Currently, the planned MMV program of this project does not include noble gases [2]. However, they may be included in ‘triggered’ environmental monitoring surveys.

Noble gases are chemically inert and their concentrations and isotopic ratios, or ‘fingerprints’, are characteristic of the fluid source [3], such that the noble gas fingerprint of a seafloor or wellbore CO<sub>2</sub> anomaly may be used to identify its origin. Ideally, for successful application, baseline concentrations of noble gases in the various fluids (e.g. injected fluids, reservoir, overburden fluids and seafloor seeps) of the whole storage complex are known.

Noble gases are found in trace amounts in captured CO<sub>2</sub> [4,5]. Noble gas fingerprints differ significantly according to the source from which CO<sub>2</sub> is captured, and resulting from the specifications of the capture process [4,5]. Hence, analysis of CO<sub>2</sub> streams from each capture plant allows the source of CO<sub>2</sub> in transportation systems (e.g. tankers, pipelines), or in the event of leaks from sub-surface facilities, to be identified. Such information may be valuable at facilities where multiple CO<sub>2</sub> sources are mixed and processed. However, as we will show, the significant depletion of noble gases in the captured CO<sub>2</sub>, and the subsequent inheritance of the noble gas signature in the reservoir, likely relieves the imminent need to monitor the noble gas composition of the capture sites continuously.

For the presented work, we sampled the gas streams during a feasibility test of a small-scale capture facility at the WtE incineration plant Klemetsrud in 2019. We present the analysis of the samples’ noble gas fingerprints. The dataset also illustrates how the capture process alters noble gas signatures.

Correct interpretation of a seafloor CO<sub>2</sub> anomaly requires knowledge of the natural background as well as physical processes potentially modifying noble gas concentrations and isotopic ratios of injected CO<sub>2</sub> during migration [e.g. 6]. We interpret the applicability of noble gases as tracers in a monitoring scheme at a storage site, by modelling the alteration of the noble gas fingerprint of the CO<sub>2</sub> through equilibration with formation water in dependence of the depth of a storage reservoir and the CO<sub>2</sub> saturation of the reservoir.

## 2. Study Site

### 2.1. WtE Plant Klemetsrud

The waste-to-energy (WtE) plant Klemetsrud is located in the municipality of Oslo, Norway, and run by Fortum Oslo Varme AS, a joint-company of Fortum and the city of Oslo. The waste consists of municipal, industrial and a minor fraction of hospital waste from Norway and abroad. The incineration properties of the waste, i.e. composition and resulting parameters such as humidity and dry heating value stay homogenous throughout the year [7]. After sorting parts of the waste for recycling, the remainder is combusted. Thereby, roughly 850 GWh/a are produced through steam turbines and heat exchangers and distributed as electrical energy and district heating resulting in 460000 tCO<sub>2</sub>/a [7]. In the future, the plant could contribute a total of 415000 tCO<sub>2</sub>/a to the Norwegian Longship project, assuming 95 % capture efficiency and 95 % uptime.

The plant has three incineration lines and air is used to supply oxygen for all three combustion processes. Flue gas treatment is the same for lines 1 and 2. Here, the flue gas is treated with calcium hydroxide and activated carbon to remove acidic and other harmful components. Urea is used to reduce nitrogen oxides. In line 3, flue gas is treated on a wet scrubber for particle removal. Here, nitrogen oxides are converted by aqueous ammonia. The resulting flue gas composition is fairly similar for all lines with a particulate matter count of 19000 nuclei/cm<sup>3</sup>. However, depending on the O<sub>2</sub> content, CO<sub>2</sub> content may vary at 10±2 % [7]. In average, flue gas composition is 13.9 vol.% H<sub>2</sub>O, 11.3 vol.% CO<sub>2</sub> and 7.3 vol.% O<sub>2</sub> with the balance comprising N<sub>2</sub>, minor components and trace elements [8].

## 2.2. Test Facility and Sampling

A small-scale capture test facility was set up at the WtE plant Klemetsrud from February to December 2019 [8]. Amine gas treatment separated CO<sub>2</sub> from the exhaust of the waste incineration. The test aimed to qualify the technology in a long-term test and assure that amine emissions are low. The schematics of the set-up are shown in Fig. 1. The exhaust from the plant, the flue gas, is brought into contact with an aqueous amine solvent in the absorber (Fig. 1). The CO<sub>2</sub> reacts with the solvent and the CO<sub>2</sub>-rich amine solution is transferred to the stripper where it is heated. As a result, the CO<sub>2</sub> is resolved as gas with a high purity in the final gas mixture.

The test facility had a capture capacity of 150 kgCO<sub>2</sub>/h and achieved a purity of 99.9+ vol.% CO<sub>2</sub> in the product. The capture efficiency was above 90 % for the majority of the test period [8].

Absorber inlet pressure was 7-10 kPa above ambient air pressure and the inlet gas temperature was 40 °C. The solvent is Shell Cansolv DC-103, a 50 wt% aqueous amine solution of otherwise confidential composition.

Samples were taken at sampling points representing the exhaust ('Flue gas') from the waste incineration, the CO<sub>2</sub> depleted flue gas ('Depleted flue gas') and the CO<sub>2</sub> product ('Captured CO<sub>2</sub>') (Fig. 1). This describes the in- and outgoing fluxes of the capture process. Samples were taken in stainless steel containers, which were flushed for several minutes, to avoid air contamination. Collection was conducted on 15.08.2019, when only gas from incineration lines 1 and 2 was fed into the absorber. Analysis was performed by the noble gas laboratory at the University of Lancaster, using a NGX noble gas mass spectrometer (Isotopx) [details e.g. in 9].

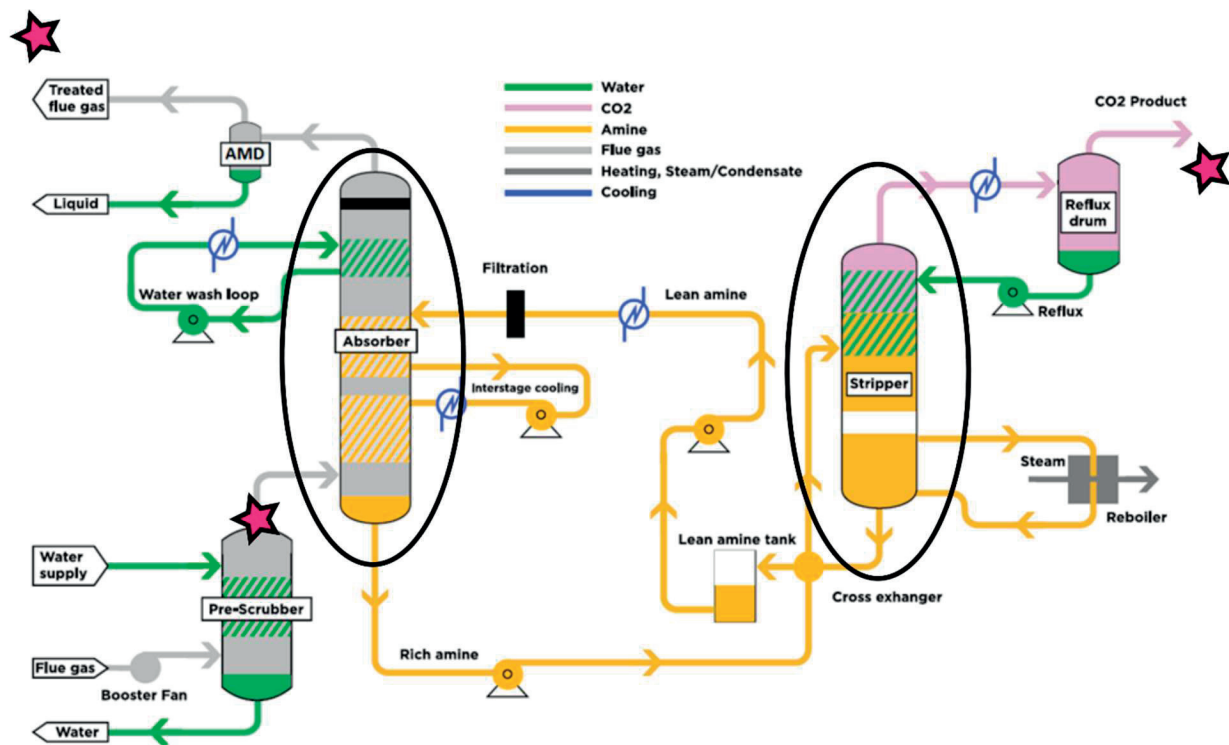


Fig. 1. Schematic set-up of the CO<sub>2</sub> capture test facility at Klemetsrud WtE plant [modified from 10]. The absorption process, from flue gas to CO<sub>2</sub> product, using amine solvents is shown, with the absorber and stripper encircled. Stars mark the three gas sampling points.

### 3. Methods

#### 3.1. Amine Gas Treatment and Noble Gases

The main on-going chemical process, the reaction of the CO<sub>2</sub> with the amines, does not affect the noble gases due to their chemical inertness. However, noble gases physically dissolve to reach equilibrium between the dissolved and the gas phase. Therefore, at equilibrium it may be possible to describe the phase partitioning in the absorber by applying Henry's law. The dissolved concentrations then depend on the partial pressure of the gas species in the gas phase and the gas specific and temperature-dependent solubility for the respective solvent (Henry's constant). Indication that Henry's law could be applied to describe dissolution at some capture plants was found in [5]. The solubilities of noble gases in amine solvents are, however, unknown. Further, at industrial sites, the exact solvent composition is often proprietary, just as at the Klemetsrud test facility.

Besides the aforementioned factors, the process design of each site, may hinder reaching equilibrium by the specific layout of, for example, the absorber column and stripper internals, the liquid withdrawal configuration and the operating pressure regimes. Further, foam can develop in the absorber due to gas bubbles stabilizing on surfactants or contaminants in the amine solvent [11]. Bubble-mediated physical gas exchange may then be an additional pathway for noble gases into the amine solvent.

Therefore, instead of Henry's constants, we define an absorption ratio to describe how the capture process affects relative concentrations of noble gases in the gas streams. This is the ratio of noble gas concentrations in the CO<sub>2</sub> product and the concentrations in the flue gas.

#### 3.2. Equilibration with Formation Water

To evaluate the change of noble gas signatures of the CO<sub>2</sub> product subsequent to injection into a storage reservoir, we calculate the phase partitioning of injected CO<sub>2</sub> in equilibrium with the formation water of a geological storage reservoir. We apply Henry's law, following the derivation in [6]. The gas concentration of a gas *i* calculates to:

$$[i]_g = [i]_T \left( \frac{22400 T \rho_{H_2O} V_{H_2O}}{18 \cdot 273 \frac{\gamma_i}{\phi_i} K_{i,CO_2-H_2O} V_{CO_2}} + 1 \right)^{-1}, \quad Eq. 1$$

with the systems total concentration  $[i]_T$  of gas *i*, water density  $\rho_{H_2O}$  at system pressure, temperature *T*, activity  $\gamma_i$  and fugacity  $\phi_i$  of the gas at system pressure and temperature, volume of water and CO<sub>2</sub>,  $V_{H_2O}$  and  $V_{CO_2}$ , respectively. The total concentration can be derived from the sum of the product of concentration in the single phases and their volumes.

Values of  $K_{i,H_2O}$ ,  $\gamma_i$  and  $\phi_i$  can be found in [6 and references therein]. The Henry's constants,  $K_i$ , of noble gases were found to deviate significantly for high density CO<sub>2</sub>-H<sub>2</sub>O systems [12]. The authors experimentally derive deviation factors,  $\kappa_i$ , for all noble gases besides Ne and Rn. This correction allows calculation of the deviation of the Henry's constants for a given gas using a three parameter dependency to the CO<sub>2</sub> density:

$$K_{i,CO_2-H_2O} = \kappa_i K_{i,H_2O} = \left( \frac{(a_i \rho_{CO_2}^2 + b_i \rho_{CO_2} + c_i)}{100} + 1 \right) K_{i,H_2O}. \quad Eq. 2$$

$K_{i,H_2O}$  is the Henry's constant at a given temperature in units of pressure for a low-pressure noble gas-water system. The upper limit for the density in the experiments of [12] was 656 kg/m<sup>3</sup>. Even though, explicitly advised against we apply this deviation also for densities up to 690 kg/m<sup>3</sup> due to lack of data.

The densities in Eq. 1 and 2 are also functions of temperature and pressure, which can be expressed as gradients of depth. Geothermal and pressure gradients may vary in different geological settings, here we use 30 °C/km and 10.18 MPa/km. We derive the densities for CO<sub>2</sub> from [13] and for H<sub>2</sub>O from [14].

Since Eq.1 is a function of the volume ratio,  $V_{H_2O}/V_{CO_2}$ , the phase partitioning can be calculated independent of an actual storage site volume. We discuss the ratio at the maximal saturation,  $S_{max}$ , of CO<sub>2</sub> for residual trapping in a



reservoir rock containing CO<sub>2</sub> and water. The CO<sub>2</sub> saturation was found experimentally to be between 13 and 92 % for several reservoir rock samples with a mean of 61 % [15].

#### 4. Results

The concentrations and isotopic ratios of the most abundant isotopes of the noble gases He, Ne, Ar, Kr and Xe at Klemetsrud are shown in Tab. 1 and 2. Further, sample signatures of the captured CO<sub>2</sub> at TCM (post-combustion), Melkøya (natural gas processing) [5] and those presented in [4] are summarized. The plants cover a range of sizes, flue gas sources and capture processes and details can be found in the given references. The studies have different data available, especially for some of the isotopic ratios. Mainly in the captured CO<sub>2</sub> concentrations can be below the analytical detection limit, as is the case for <sup>3</sup>He/<sup>4</sup>He in this study (noted with n.d.).

Table 1. Concentrations in cm<sup>3</sup><sub>STP</sub>/cm<sup>3</sup><sub>STP</sub> of the most abundant isotopes in samples from the Klemetsrud WtE plant are given including uncertainty of one standard deviation. For comparison, observed concentration ranges at TCM and Melkøya [5] as well as the range of six other sites presented in [4] are given (without uncertainties).

Samples Name	<sup>4</sup> He	<sup>20</sup> Ne	<sup>40</sup> Ar	<sup>84</sup> Kr	<sup>132</sup> Xe
Atmosphere	5.24E-06	1.82E-05	9.34E-03	1.14E-06	2.34E-08
<b>Klemetsrud Waste Incineration</b>					
Flue gas	2.26E-06±3.19E-08	4.50E-08±6.38E-10	4.85E-04±6.88E-06	1.56E-08±2.25E-10	1.35E-10±1.94E-12
Depleted flue gas	2.74E-06±3.88E-08	5.40E-08±7.67E-10	9.38E-08±1.46E-10	1.56E-08±2.25E-10	1.71E-10±2.45E-12
Captured CO <sub>2</sub>	6.28E-09±9.74E-11	5.88E-11±8.34E-13	3.71E-10±5.41E-12	3.64E-12±5.4E-14	1.13E-13±1.68E-15
<b>TCM, Natural Gas Combustion</b>					
Captured CO <sub>2</sub>	1.7 - 3.3E-09	4.3E-09	3.7 - 4.8E-06	0.7-1.0E-09	1.2 - 1.8E-10
<b>Melkøya, Natural Gas Processing (no combustion)</b>					
Captured CO <sub>2</sub>	2.9E-06	1.8E-09	1.0E-06	5.3E-11	3.7E-11
<b>Range of Several sites presented in Flude et al.</b>					
Captured CO <sub>2</sub>	2.29E-09 - 3.64E-07	2.64E-09 - 4.27E-07	4.33E-06 - 1.37E-04	3.59E-10 - 6.34E-09	2.82E-11 - 1.91E-09

Table 2. Isotopic ratios in samples collected at Klemetsrud with uncertainty of one standard deviation. For the captured CO<sub>2</sub> the observed range at TCM, Melkøya [5] and the range of six sites presented in [4] is given for comparison if available. Those are given without uncertainty.

Samples Name	<sup>3</sup> He/ <sup>4</sup> He	<sup>20</sup> Ne/ <sup>22</sup> Ne	<sup>21</sup> Ne/ <sup>22</sup> Ne	<sup>40</sup> Ar/ <sup>36</sup> Ar	<sup>38</sup> Ar/ <sup>36</sup> Ar	<sup>86</sup> Kr/ <sup>84</sup> Kr	<sup>132</sup> Xe/ <sup>129</sup> Xe	<sup>132</sup> Xe/ <sup>131</sup> Xe
Atmosphere	1.34E-06	9.78	0.029	296	0.188	0.30	1.019	1.267
<b>Klemetsrud Waste Incineration</b>								
Flue gas	2.46E-06±7.57E-08	9.7±0.2	2.87E-02	401±8	0.217±0.004	0.31	1.036	1.262
Depleted flue gas	2.48E-06±6.97E-08	9.8±0.2	2.86E-02	394±12	0.221±0.004	0.31	1.024	1.268
CO <sub>2</sub> product	n.d.	9.9±0.2	2.97E-02	308±6	0.19±0.01	0.31	1.008	1.262
<b>TCM Natural Gas Combustion</b>								
CO <sub>2</sub> product	9.35E-07	9.8		360		0.31		
<b>Melkøya Natural Gas Processing</b>								
CO <sub>2</sub> product	2.84E-08					0.25		
<b>Range of Several sites presented in Flude et al.</b>								
CO <sub>2</sub> product	4.92E-07 - 2.37E-06	9.638 - 10.263	0.028 - 0.030	284 - 299	0.0116 - 0.185			

## 5. Discussion

### 5.1 Capture Process

#### 5.1.1. Absorption

The capture process leads to low noble gas concentrations in the captured CO<sub>2</sub> (Tab. 1). The absorption ratio (see Sec. 3.1) allows to evaluate the impact of the capture process on the different gas species and in comparison to other sites. In Fig. 2, the absorption ratios of the Klemetsrud capture test are plotted in comparison with these at Melkøya natural gas processing plant and TCM, a post-combustion plant two large-scale Norwegian capture sites [3]. The noble gases are affected differently at different capture plants. Especially, significantly less Ar is transferred into the CO<sub>2</sub> product at Klemetsrud compared to the other noble gases and compared to other sites (Tab. 1). In addition, Kr and Xe exhibit lower ratios at Klemetsrud compared to TCM and Melkøya, while He and Ne plot in between. There is no uniform solubility trend with increased solubility of heavier noble gases, as found at TCM (yellow bars).

There is a lack of data for the solubility of noble gases in such solvents. It may be possible to estimate the solubility in salt solutions through a Schumpe model [16]. Given that, ionic strength, which is related to the CO<sub>2</sub> load and degradation of a solvent at a given point in time, influences solubility at the test facility. At the time of sampling at Klemetsrud the degradation was already significantly progressed and at a normal operational site the amine solution would likely have been renewed [10]. This may be a factor in the differences of the absorption ratios between the different sites, besides foaming and incomplete equilibrium (Fig. 2).

In a recent work [17], O<sub>2</sub> solubility in several amine compositions was measured to be fairly similar to that in water, with temperature having a stronger impact than the amine composition. These results would have to be confirmed for noble gases. For O<sub>2</sub> it was further observed that in some configurations the CO<sub>2</sub> loading can significantly lower O<sub>2</sub> solubility [17]. It is argued that chemical reactions outplay physical gas transfer [17]. Such a competition, however, is not found for the inert noble gases.

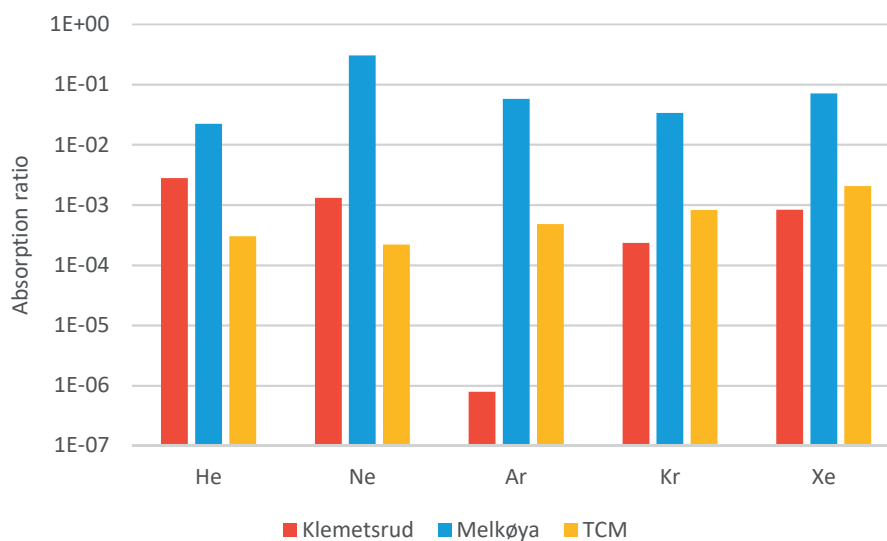


Fig. 2. Absorption ratio (ratio of 'Captured CO<sub>2</sub>' and 'Flue Gas') for the Klemetsrud WtE capture facility from this study in comparison to the Melkøya natural gas processing plant and TCM in [5].

### 5.1.2. Concentrations compared to other locations

Noble gas concentrations in the captured CO<sub>2</sub> are plotted in comparison to the values observed at other capture sites (Fig. 3 left) and to atmospheric values (right). The sample from Klemetsrud shows low He concentrations, but within the range observed at other capture sites. All other noble gas concentrations (Ne, Ar, Kr, Xe) are exceptionally low. This could be caused by the discussed solubility effect by the advanced degree of degradation and the high purity of the CO<sub>2</sub> reached during the absorption process in the test set-up. Isotopic ratios of the elements (not depicted) are similar to air, since noble gases are introduced significantly through the air being used for combustion of the waste.

The absorption process does not significantly fractionate the isotopic ratios of individual noble gases (Tab. 2). However, there is variation in the fractionation of elemental noble gas ratios between the flue gas and captured CO<sub>2</sub> and between different sites (e.g. Ar/He, Xe/He) (see also Fig. 2).

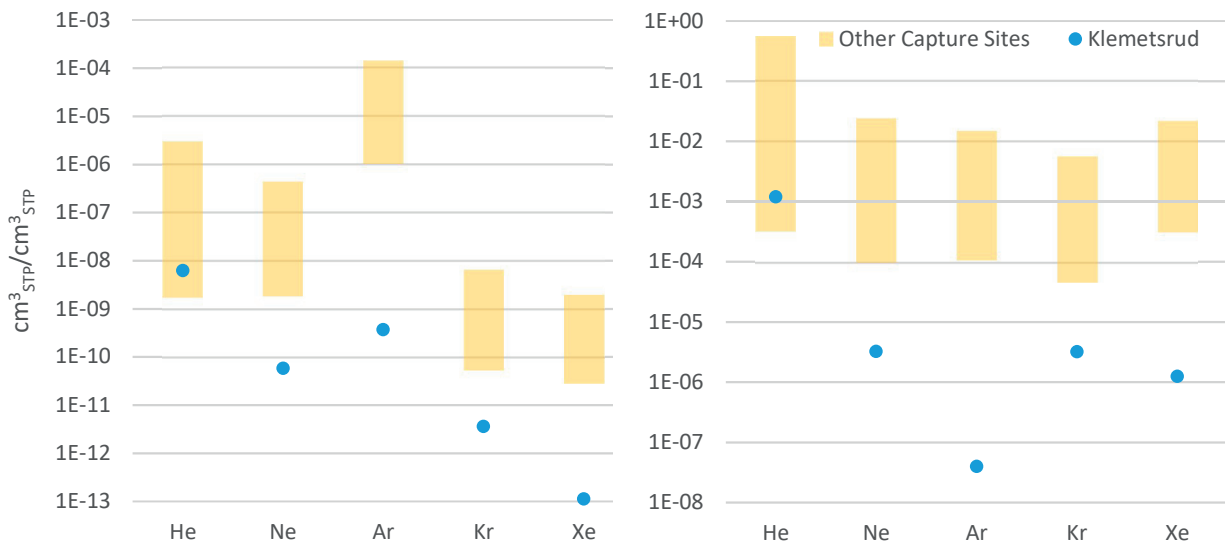


Fig. 3. Left: Noble gas concentrations at Klemetsrud (blue dots) compared to the ranges found at other capture sites (data from [4,5] listed in Tab. 1). Right: The same concentrations and ranges relative to atmospheric values.

## 5.2. Detectability of Captured CO<sub>2</sub>

### 5.2.1. Equilibration with formation water

Noble gas concentrations in the captured, and subsequently to be injected, CO<sub>2</sub> are typically low in comparison to other background fluids due to the CO<sub>2</sub> absorption process (Tab. 1, Fig. 3). Critically, noble gases in the pure captured CO<sub>2</sub> are significantly different to the natural background signatures of reservoir fluids, which will have a predominately crustal signature [6,18].

We apply phase partitioning calculations that would occur after injection and during migration to model if the signature of the captured CO<sub>2</sub> is maintained. In the storage complex, these background fluids on a migration pathway from reservoir to surface would include formation water, natural gas and oil, subsea gas seeps, ocean water and finally the atmosphere. Formation water and natural gas/oil exhibit crustal noble gas signatures with a typically minor mantle noble gas signature contribution [18]. The enrichment of radiogenic noble gases, <sup>4</sup>He, <sup>21</sup>Ne and <sup>40</sup>Ar is dependent on the geological setting and on the amounts of the radioelements K, Th and U in the rock [18]. Here, we use the same concentrations and parameters for the formation water as described in [5].

After injection, the CO<sub>2</sub> will equilibrate with the formation water. Since the injected CO<sub>2</sub> is depleted in noble gases, it will strip gases from the formation water. The degree of noble gas enrichment in stored CO<sub>2</sub> is dependent on the volume ratio of gas and water (Eq.1). The enrichment is different for the different noble gases since some factors, e.g.

Henry's constants, in Eq. 1 and Eq. 2 are gas specific. Further, values will vary with depth according to local geothermal and pressure gradients.

Fig. 4 shows the concentration of the injected CO<sub>2</sub> in dependency of the gas-water volume ratio and relative to a value at  $V_g/V_w=0.0001$  at 2000 m depth. It becomes apparent that the concentrations in the injected CO<sub>2</sub> are only influential at high  $V_g/V_w$ .

$S_{max}$ , the irreducible water content, may be considered as the ratio that is most in favor of maintaining the injected CO<sub>2</sub> depleted signature meanwhile still being realistic to occur. Here, concentrations of the noble gases are 80-90% of that of the formation water value (Fig. 4). This range derives from (1) the concentration in the injected CO<sub>2</sub> and (2), and more significantly, differences in the solubility. For example, He, the least soluble gas, is stripped more effectively from the water into the gas phase and injected CO<sub>2</sub> will be closer to formation water values. This enrichment is not considerably affected by the concentrations in the captured CO<sub>2</sub> for gas-water volume ratios at realistic levels, as long as the concentrations are significantly lower than in the background of the formation water.

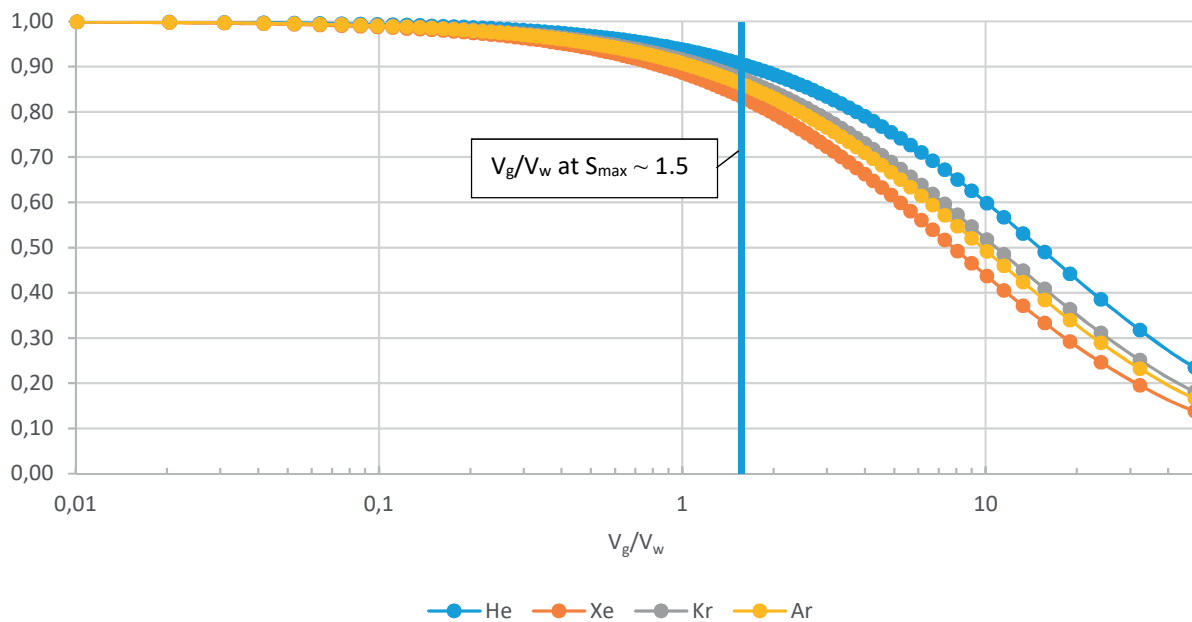


Fig. 4. Phase partitioning of the CO<sub>2</sub> from Klemetsrud with formation water with a crustal signature. Up to realistic gas-water volume ratios the formation water signature prevails.

### 5.2.2. Depth dependency

Fig. 5[a] shows the ratio of the concentration of a noble gas in the captured CO<sub>2</sub> and in the CO<sub>2</sub> that has equilibrated with the formation water in dependence of depth. All noble gases are being enriched by at least three orders of magnitude, at  $S_{max}$ , throughout the depth profile. This will also lead to isotopic ratios being largely inherited from the formation. Slight gas specific differences can lead to elemental ratios being fractionated. The enrichment is changing over depth, which is more pronounced depicted when showing the ratio of the concentration at 1000 m and the concentration at given depth (Fig. 5[b]). He, less enrichment with depth, and Xe, more enrichment with depth, are most significantly impacted by depth, i.e. temperature and pressure, changes. However, over depth the general conclusion of significant enrichment is maintained (Fig. 5[a]).

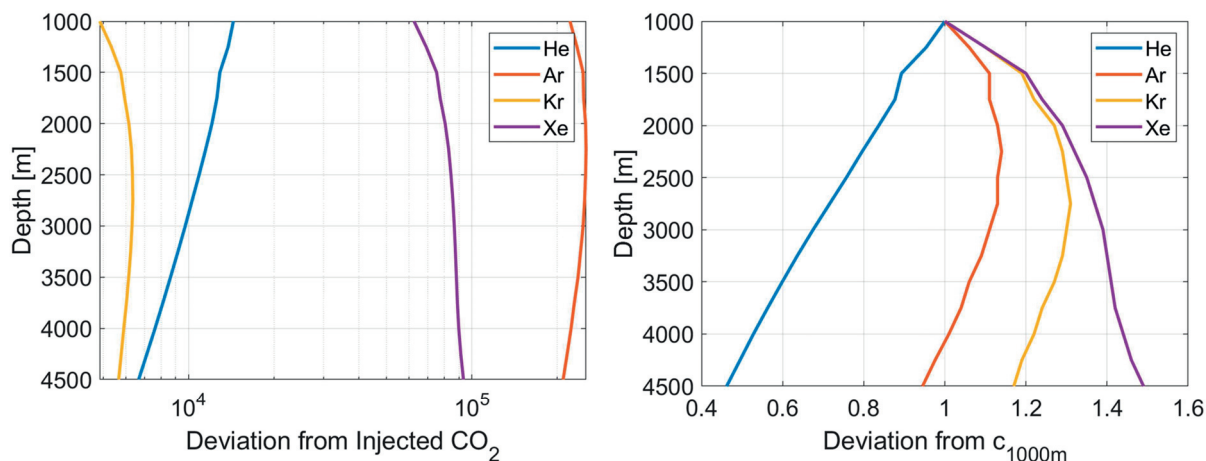


Fig. 5. Depth dependency of the enrichment of the injected CO<sub>2</sub> at  $S_{max}$ . [a] Ratio of concentration in the CO<sub>2</sub> after injection and in equilibrium with formation water with a crustal signature and the captured CO<sub>2</sub> at Klemetsrud. [b] Ratio of the concentration at 1000 m to the concentration at given depth.

### 5.2.3. Implication for monitoring

The CO<sub>2</sub> is enriched with noble gases for realistic volume ratios, assuming equilibrium is reached. The question remains if full equilibration is realistic. We approach this phenomenologically. A CO<sub>2</sub> plume would migrate after maximum saturation is reached. Assuming it has not fully equilibrated it then gets in contact with originally, noble gas rich formation water. This will be repeated during further migration. The noble gas signature will, therefore, especially at the front of a plume be enriched. Further, the maximum saturation ratio results from residually trapped water that cannot be displaced, which will release its noble gas content inside a CO<sub>2</sub> plume, hence, noble gas free CO<sub>2</sub> parts will be rare.

The inheritance of the crustal fingerprint of the formation may make the discrimination of leaked CO<sub>2</sub> from other deeply derived fluids with a similar signature challenging, which will have to be evaluated in more detail. However, by coupling high precision measurements of the noble gas elements and isotopic ratios to other elemental ratios such as CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub> or stable isotopes in the sampled gases, diagnostic fingerprinting becomes more likely.

At the offshore storage prospect for the Norwegian Longship project, there is natural gas and oil contained in nearby reservoirs, i.e. the Troll Field, which also has a crustal signature. Here, mentioned elemental ratios would help to specify a crustal source. Discrimination of CO<sub>2</sub> leaking from the storage site versus CO<sub>2</sub> from shallow gases (e.g. submarine groundwater discharge, biogenic gas, decomposing hydrates etc.) would be relatively straight forward, due to the distinct noble gas compositions. Shallow gas hydrate seeps, for example, were found to have a distinct fractionation, with enrichment towards heavier noble gases [19]. Shallow groundwater sources may have atmospheric signatures with only minor radiogenic enrichment.

## 6. Conclusion

In this work, we analysed the gas streams at the WtE Klemetsrud capture test facility, which may be a CO<sub>2</sub> source for the Norwegian full-scale CCS project, for their noble gas content:

- The captured CO<sub>2</sub> at Klemetsrud exhibits lower noble gas concentrations than previously observed at other capture facilities. Isotopic ratios are air-like, due to air being introduced during combustion. Since absorption varies for the different noble gases distinct elemental ratios are imprinted. The low values may be explained by the specifications of the confidential solvent or the CO<sub>2</sub> load and ionic strength of the solvent at the time of sampling. During sampling in this study, the degradation was already quite advanced and therefore high ionic strength reduces the physical solubility of gases in the solvent. This may not be the case in the typical production window of degradation during actual plant operation.

For evaluation of a CO<sub>2</sub> storage site, characterization of the background fluids, including the captured CO<sub>2</sub>, is essential. This work contributes to that goal and with analogue concentrations from formation water, we model applicability of noble gas tracers in a future monitoring scheme:

- The modelling suggests that, once the CO<sub>2</sub> is injected, it will strip gases from the formation water, thereby virtually inheriting the signature of the formation, with only minor effects from gas-specific solubility and noble gas signature of the injected CO<sub>2</sub>. The crustal signature allows for targeted monitoring and differentiation against atmospheric/shallow gas signatures, but likely hinders differentiation of fluids with similar crustal signature. To make these distinctions possible, comprehensive baseline characterization of the different fluids in the storage site system and especially at the seafloor, i.e. sediments and already active fluid seepages, is crucial.

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### **A.3 On the Distinctiveness of Noble Gases in Injected CO<sub>2</sub> from Background Fluids**

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**Summary** In this conference contribution the background fluid signatures that may be realistic for a North Sea storage site are collected. This includes a review of natural gas signatures in the North Sea. Then phase partitioning is applied to injected CO<sub>2</sub>. The resulting signature is used for mixing calculations to demonstrate how different these signatures are from each other, even without tracer addition.

An example for a tracer addition is shown over a range of water gas volume ratios. The dependency of the resulting concentrations on the water gas volume ratios, underlines that interpreting results at the maximum saturation ratio is a best case scenario. At maximum saturation the concentrations are most deviating from the background or the amount of a tracer needed to be added is smallest. Paper III expands this work by considering natural variability of the observed signatures and the measurement uncertainty. This constrains the mixing calculations further.





## ON THE DISTINCTIVENESS OF NOBLE GASES IN INJECTED CO<sub>2</sub> FROM BACKGROUND FLUIDS

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### Abstract

A comprehensive monitoring program for CO<sub>2</sub> storage sites is an integral part of designing CCS projects. Once a CO<sub>2</sub> anomaly is observed or suspected, the source of the CO<sub>2</sub> may be identified through evaluation of geochemical tracers. Noble gases are one of those geochemical tracers that display unique signatures for the environmental reservoirs involved in the storage site system.

The background fluids at storage prospect, such as formation water, hydrocarbons or shallow gases need to be characterized prior to injection. Typical noble gas signatures are of atmospheric, crustal/radiogenic or mantle character. Captured CO<sub>2</sub> can contain a large range of noble gas concentrations and ratios with typically significantly lower concentrations than the other background fluids.

Here, we collect the noble gas analysis of various environmental fluids in the storage site system relevant to the North Sea, such as hydrocarbons and shallow gases, to narrow down possible observable signatures. If samples are not available realistic values can be inferred from analogue sites/studies. Further, we show that after injection, phase partitioning, hence equilibration, of the injected CO<sub>2</sub> with formation water leads to adaption of a radiogenic signature from the formation water. Therefore, the initially low concentrations of the CO<sub>2</sub>, and their associated elemental and isotopic ratios, are only preserved when remaining almost pure. These signatures can be applied to mixing calculations with the background fluids to rule out if injected CO<sub>2</sub> is contributing to an anomaly.

Meanwhile, noble gases are one of the environmental tracers that could be cost-effective since they are naturally inherent in the CO<sub>2</sub> and the storage reservoir fluids, we also model the addition of artificial noble gas tracers to increase the detectability, i.e. ability to recognize lower contributions of injected CO<sub>2</sub> in a background reservoir fluid. These calculations can be fed into cost calculations to estimate the economic impact of such an additional monitoring measure.

**Keywords:** *Monitoring and Verification, Noble gases, Tracer addition*

### 1. Introduction

Designing a CO<sub>2</sub> storage sites measurement, monitoring and verification (MMV) program is an essential part of a CCS project [1]. The Norwegian ‘Longship’ project aims to store CO<sub>2</sub> in the ‘Aurora’ prospect in the North Sea in the vicinity of the Troll oil and gas field. The planned, continuous MMV program does not include noble gases [2], however, with the content of ‘triggered’ environmental monitoring surveys not yet defined, this may be included there.

Noble gases are trace constituents of most environmental fluids. The concentrations of He, Ne, Ar, Kr, Xe, and their isotopic ratios constitute a signature or ‘fingerprint’ of a fluid. Due to their inertness, only physical processes influence them such that they have widespread application in deciphering physical and geochemical processes [3]. Inherent noble gas tracers were used to refute an alleged leakage from a CO<sub>2</sub> storage site [4].

The main groups of noble gas fingerprints are of atmospheric [5], crustal [6] and mantle character [7]. However, there are wide isotopic concentration ranges within these categories, such that characterizing the

background fluids of a storage site is key for the applicability of noble gases as tracers. Therefore, the ICO<sub>2</sub>P project has characterized the signature of various captured CO<sub>2</sub> streams [8,9,10]. Noble gases showed large variation at the different sample sites and all were being depleted through the CO<sub>2</sub> capture process in a way that the captured CO<sub>2</sub> has a low noble gas content compared to other background fluids (e.g. natural gas). For background fluids at the ‘Aurora’ storage site noble gas samples have not yet been analyzed such that analogue studies e.g. describing other hydrocarbon systems in the North Sea can be used to infer the noble gas content.

One also has to consider that the CO<sub>2</sub> can undergo interaction with e.g. in-situ formation water or gases, subsequently altering the noble gas fingerprint. In previous work [8,9], we showed that the phase partitioning with formation water leads to the stripping of gases and inheritance of a radiogenic signature. We concluded that this provides a monitoring target in differentiating injected, “anthropogenic” CO<sub>2</sub> from shallow, natural CO<sub>2</sub> sources, e.g. biogenic or gas hydrates.

In this work, we build the foundation of noble gas signatures that may be expected for the North Sea and follow up previous calculations with mixing calculations of the injected, equilibrated CO<sub>2</sub> with other fluids possibly involved in anomalies.

Further, we apply the calculations to a simulated addition of noble gas tracers. This can increase the distinctiveness of the injected CO<sub>2</sub> relative to natural fluids. However, this comes with a cost, which can be estimated from an economic analysis including the tracer gas amounts needed and the related gas prices.

## 2. Baseline Concentrations

Collecting the baseline concentrations of fluids in the storage site system allows assessing differentiability of the background to injected CO<sub>2</sub>. Tab. 1 shows a summary of the expected ranges for different environmental fluids.

Captured CO<sub>2</sub> has been analyzed for several capture plants in Norway [8,9,10] and other countries [11]. Noble gas concentrations are typically low and the isotopic signatures are either air-like for plants with combustion prior to capture (e.g. waste incineration) or natural gas-like (e.g. natural gas processing).

For natural gas, sample analyses for the North Sea are currently available for Sleipner Vest and the Magnus field [12,13]. The results show a typical radiogenic character, deriving from the production of <sup>4</sup>He, <sup>21</sup>Ne and <sup>40</sup>Ar through radioactive decay of the elements K, U and Th in the rocks [6]. Samples for natural, geologic CO<sub>2</sub> have a dominantly magmatic (mantle) signature with subsequent equilibration with radiogenic formation water. The values in Tab. 1 are from large natural CO<sub>2</sub> systems in the US [14,15]. Natural CO<sub>2</sub> in the North Sea context is typically a minor constituent of natural gas accumulations [e.g. 12] and would therefore likely have the same concentrations of associated noble gases as natural gas.

Radiogenic signatures can cover a large range since the amount of a noble gas isotope in subsurface reservoirs; natural gas, oil, natural CO<sub>2</sub> or in pore water, is dependent

on the exchange with other fluids from the atmosphere, crust and mantle. Further, longer time of separation from other reservoirs allows for more radiogenic accumulation. The provenance of natural gas can also have an impact i.e. stripping of noble gases during migration through formation water.

Close to the seabed gas hydrates may occur. Only elemental gas concentrations have been analyzed for gas hydrates but not the isotopic composition [16]. Those samples were collected outside the coast of Oregon, US and showed a quite specific fractionation pattern with preferential incorporation of heavier noble gases and suppression of the lighter ones (Tab. 1).

Sediment samples, i.e. the dissolved noble gases in the sediments' pore-water, are rare and for the North Sea there is no data set available. Sediment pore water concentrations are dependent on the temperature during sedimentation and if there are leakage sites, e.g. black smokers, nearby. The data from [17,18] has to be seen in the context of continental plate boundaries which may therefore not be representative for the North Sea.

Seawater, if not in the vicinity of specific fluid releases, is typically air equilibrated water at a given temperature and salinity [19]. This means atmospheric gas, including noble gases, is dissolved based on the solubility of the respective gas species at these conditions in water. In case there are seepages, ocean currents may redistribute them fast, so anomalies can be local. The atmosphere is typically well mixed and has a set noble gas signature [5].

With regards to isotopic ratios there are the three main signatures and fluids represent mixtures of these to various degrees. Typical values for the isotopes mainly affected are shown in Tab. 2.

For captured CO<sub>2</sub> the ratios are dependent on the source of flue gas and if combustion has taken place prior to capture, e.g. at heat and power plants. Combustion typically introduces noble gases from the air also shifting

Table 1: Observed noble gas concentrations for the different fluids in the storage site systems. Captured CO<sub>2</sub> from several sites [8,11]. Atmospheric values from [5]. Seawater concentrations after [19] (assuming a temperature of 7,5 °C and a salinity of 34,2 g/L). Natural gas for He, Ne and Ar compiled from the Sleipner field and Magnus oil field in the North sea from [12,13], Kr and Xe from Sleipner Field [12]. Natural CO<sub>2</sub> compiled from [14] and [15]. Sediment values from the South Pacific Ocean [17] and the Mediterranean ridge for helium [18]. Gas hydrates from [16].

	He	Ne	Ar	Kr	Xe
<b>Captured CO<sub>2</sub></b>	2,29E-09 – 2,9E-06	6E-11 – 4,27E-07	3,7E-10 – 1,4E-04	3,6E-12 – 6,3E-09	1,1E-13 – 1,9E-09
<b>Natural CO<sub>2</sub></b>	1E-04 – 1E-02	7,0E-08 – 1,8E-06	1,5E-05 – 2,7 E-05	1,0E-10 – 1,0E-08	5,0E-12
<b>Natural Gas</b>	5E-03 – 1,3E-04	0,8E-08 – 2,7E-08	1,5E-05 – 2,7E-05	9,5E-09	2,0E-09
<b>Gas Hydrates</b>	7,0E-10 – 9,0E-10	2,5E-09 – 6,2E-08	3,5E-05 – 5,3E-04	1,8E-08 – 3,0E-07	2,7E-09 – 9,4E-08
<b>Sediment (cm<sup>3</sup>/g)</b>	1,0E-04 – 1,0E-02	5,0E-09 – 5,0E-07	1,0E-05 – 1,0E-08	5,0E-08 – 1,5E-09	8,0E-09 – 1,7E-08
<b>Seawater (cm<sup>3</sup>/g)</b>	4,0E-08	5,7E-09	1,1E-06	8,5E-08	1,1E-08
<b>Atmosphere</b>	5,24E-06	1,82E-05	9,34E-03	1,13E-06	8,7E-08

	<sup>3</sup> He/ <sup>4</sup> He (R/R <sub>A</sub> )	<sup>21</sup> Ne/ <sup>22</sup> Ne	<sup>40</sup> Ar/ <sup>36</sup> Ar	<sup>86</sup> Kr/ <sup>84</sup> Kr	<sup>132</sup> Xe/ <sup>130</sup> Xe
<b>Atmospheric Signature</b>	1	0,029	296	0,303	6,61
<b>Crustal signature</b>	~0,1	~0,033	~455	~0,303	~6,61
<b>Mantle signature (MORB)</b>	8	0,06	~30000	-	-

Table 2: Isotopic ratios for the main signatures: atmospheric [5], crustal [6], hence radiogenic, and mantle [7]. If “~”- sign averaged from several samples.

ratios towards atmospheric values. At natural gas processing sites the radiogenic ratios are maintained [8].

Noble gas ratios associated with hydrocarbons are dependent on the geological setting of a reservoir and the provenance of the natural gas. In Tab. 2 isotopic ratios are shown for the North Sea [12]. However, especially the <sup>3</sup>He/<sup>4</sup>He and <sup>40</sup>Ar/<sup>36</sup>Ar ratio can be quite varying, e.g. natural gas from Snøhvit has an order of magnitude lower value for the He ratio [8].

### 3. CO<sub>2</sub> Signature after Injection

#### 3.1 Phase Partitioning

We calculated phase partitioning with formation water that would occur after CO<sub>2</sub> injection and during migration in [8,9]. We showed that the depleted signature of the captured CO<sub>2</sub> is not maintained, but in contrast largely inherited from the formation water by gas stripping. Thereby, the CO<sub>2</sub> adopts a radiogenic signature.

In [8,9] we derived the assumed formation water concentrations based on assuming equilibrium of the water with natural gas of the Snøhvit Field. Since Snøhvit is located in a different geological setting compared to prospective sites in the North Sea, the noble gas accumulation is expectedly larger in the Snøhvit Field than in the North Sea. Therefore, in this work, we used the values from the Sleipner Field [12] to calculate the concentrations at the given gas-water ratios, V<sub>g</sub>/V<sub>w</sub>.

By calculating the ratio of the concentrations in the CO<sub>2</sub> relative to the concentrations at very low V<sub>g</sub>/V<sub>w</sub>, it becomes apparent that the formation water signature dominates up to high gas-water ratio (Fig. 1). The most relevant value for V<sub>g</sub>/V<sub>w</sub> is the maximum water saturation, S<sub>max</sub> which is approximately at 1,5. Here, no more water can be replaced by CO<sub>2</sub>. At the maximum water saturation, S<sub>max</sub>, concentrations constitute 80-90% of that of the formation. The slight differences for the enrichment for the single gases derives from gas specific solubilities.

Only at very high V<sub>g</sub>/V<sub>w</sub> the concentrations of the injected CO<sub>2</sub> will be influential without tracer addition. However, this is likely not possible to be achieved considering maximum saturation. In a scenario where an area of a reservoir is repeatedly flushed by CO<sub>2</sub> significant parts of the original noble gas content could have been stripped, thereby making the signature of the injected CO<sub>2</sub> more influential or possible to be approached. This could for example be the case at CO<sub>2</sub>-EOR (enhanced oil recovery).

#### 3.1 Tracer Addition

The adopted signature of the formation water into injected CO<sub>2</sub> allows differentiation from fluids that do not have a radiogenic signature, i.e. shallower sources (see Tab. 1). The approach of modelling phase partitioning also allows to evaluate the active addition of a noble gas tracer to the injection stream with the goal to

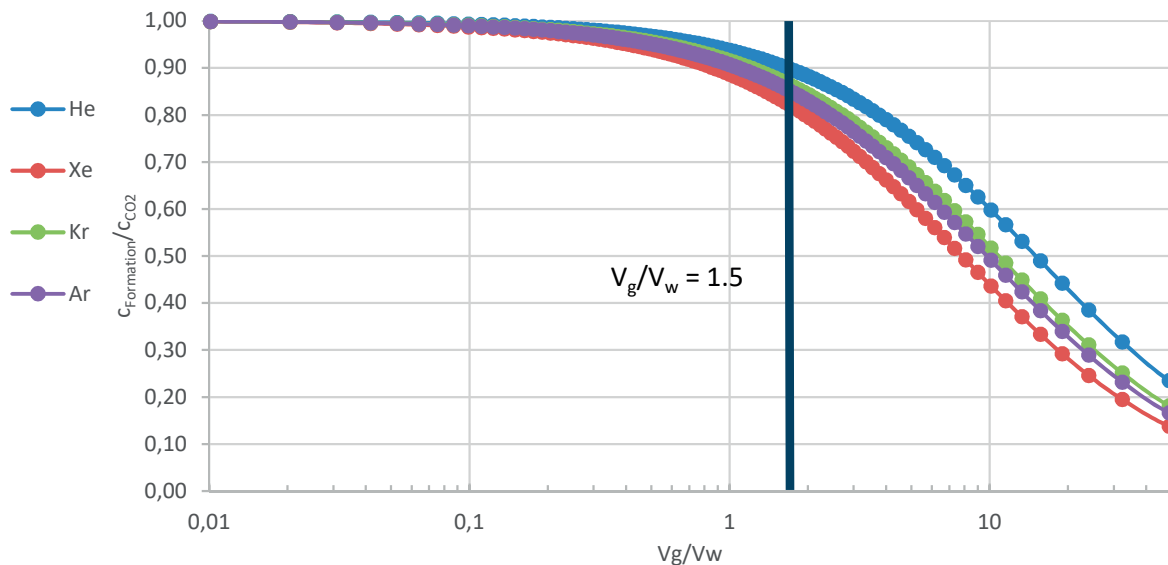
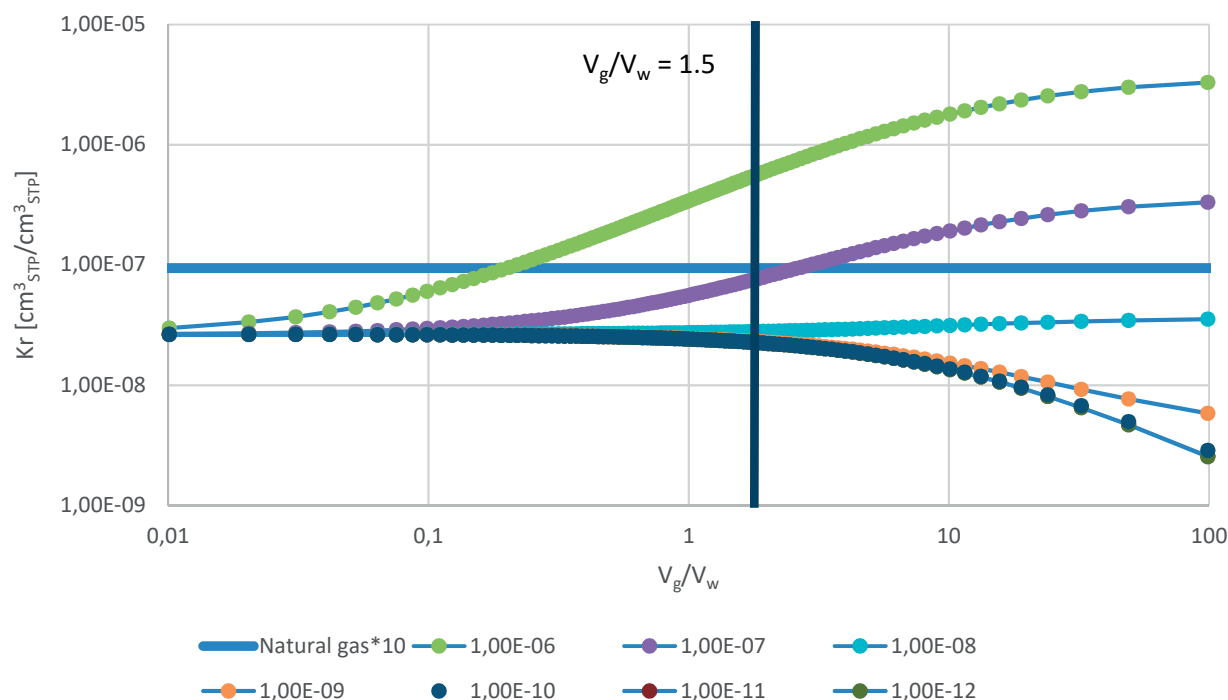


Figure 1: Phase partitioning of captured CO<sub>2</sub> from Klemetsrud, containing trace amounts of noble gases, with formation water with a crustal signature (equilibrated with natural gas from Sleipner. Concentration in the CO<sub>2</sub> relative to concentrations at a V<sub>g</sub>/V<sub>w</sub> of 0.0001. Modified from [9]. Up to realistic gas-water volume ratios, the formation water signature prevails.

Figure 2: Tracer concentration in injected CO<sub>2</sub> after equilibration for the addition of an artificial tracer; Kr in this example, in the injected CO<sub>2</sub> in dependence of V<sub>g</sub>/V<sub>H<sub>2</sub>O</sub>. Lines represent values for a tracer in the given order of magnitude. Between magnitudes 5E-07 – 1E-06 cm<sup>3</sup><sub>STP</sub>/cm<sup>3</sup><sub>STP</sub> an added tracer would be one order of magnitude above natural gas concentration at S<sub>max</sub> = V<sub>g</sub>/V<sub>w</sub> = 1.5.



maintain a significant different noble gas signature after the equilibration.

Kr and Xe are especially relevant choices for noble gas tracer addition, since they have low concentrations in background (see Tab. 1) and do not impact the main features of the radiogenic signature, in contrast e.g. to He. This could be used to differentiate the injected CO<sub>2</sub> from natural gas that may be in the vicinity of a storage site, as is the case at ‘Aurora’ [2].

For the addition of elemental Kr the resulting noble gas concentrations are modelled in dependence of V<sub>g</sub>/V<sub>w</sub> for a range of concentrations in the injected CO<sub>2</sub> (Fig.2). To achieve a value of one order of magnitude above the background in natural gas, to be significantly distinctive, an addition of Kr with concentrations in the injected CO<sub>2</sub> of 5E-07 – 1E-06 cm<sup>3</sup><sub>STP</sub>/cm<sup>3</sup><sub>STP</sub> is necessary at maximum saturation (S<sub>max</sub>). At ratios lower than S<sub>max</sub>, the background formation fluid signature prevails despite higher tracer concentrations. The same calculation leads to 5E-08 – 1E-07 cm<sup>3</sup><sub>STP</sub>/cm<sup>3</sup><sub>STP</sub> for Xe.

The value of one order of magnitude above a background, in this case natural gas, to reach distinctiveness is an arbitrary choice. It shall account for uncertainties in background concentrations and that a leakage may be a mixture of gases, where the CO<sub>2</sub> is a minor component.

The necessary amounts of a trace gas can be scaled up to a storage sites injection volume to derive the cost of such a tracer addition [20]. Including the single isotopes of the respective noble gas may reduce the amounts needed during injection. For example, <sup>3</sup>He is significantly less abundant in the environment than <sup>4</sup>He. This lower

abundance, however, typically comes with increased production cost of the respective isotope [20].

#### 4. Mixing calculations

Having established the background concentrations (Sec. 2, Tab. 1 and 2), the concentration the captured CO<sub>2</sub> will likely adopt and the potential signature of a tracer addition. Mixing calculations can be performed to estimate the content of injected CO<sub>2</sub> in a fluid. This could for example be conducted on samples from bubbling gas on the seafloor or the production stream of a natural gas field. Once an anomaly is observed noble gas mixing calculations can be applied for leakage attribution.

The noble gas concentrations of a reservoir can vary significantly (Tab. 1). By depicting the values of some of the known signatures on a crossplot it becomes apparent that several orders of magnitude are covered (Fig. 3). Fig. 3 shows the elemental ratio of Xe/He versus Xe for the different background fluids on a double logarithmic scale. He and Xe were chosen due to the low background of Xe and the typically large difference in He between crustal and shallow signatures (Tab. 1). The addition of 1E-07 cm<sup>3</sup><sub>STP</sub>/cm<sup>3</sup><sub>STP</sub> Xe to the injected CO<sub>2</sub> would distinct the signature of the CO<sub>2</sub> after injection from the pure natural gas even further as shown in Fig. 3. Then He would still allow distinction to shallow signatures.

Three mixing calculations are performed in Fig. 3, one for mixing of injected and equilibrated CO<sub>2</sub> with atmosphere and mixing with gas hydrates to illustrate the content of CO<sub>2</sub> in a mixture being needed to change the elemental ratio. The values are derived from the binary mixture of the two end-members for a given percentage of CO<sub>2</sub> in the fluid mixture. Such an analysis, however,

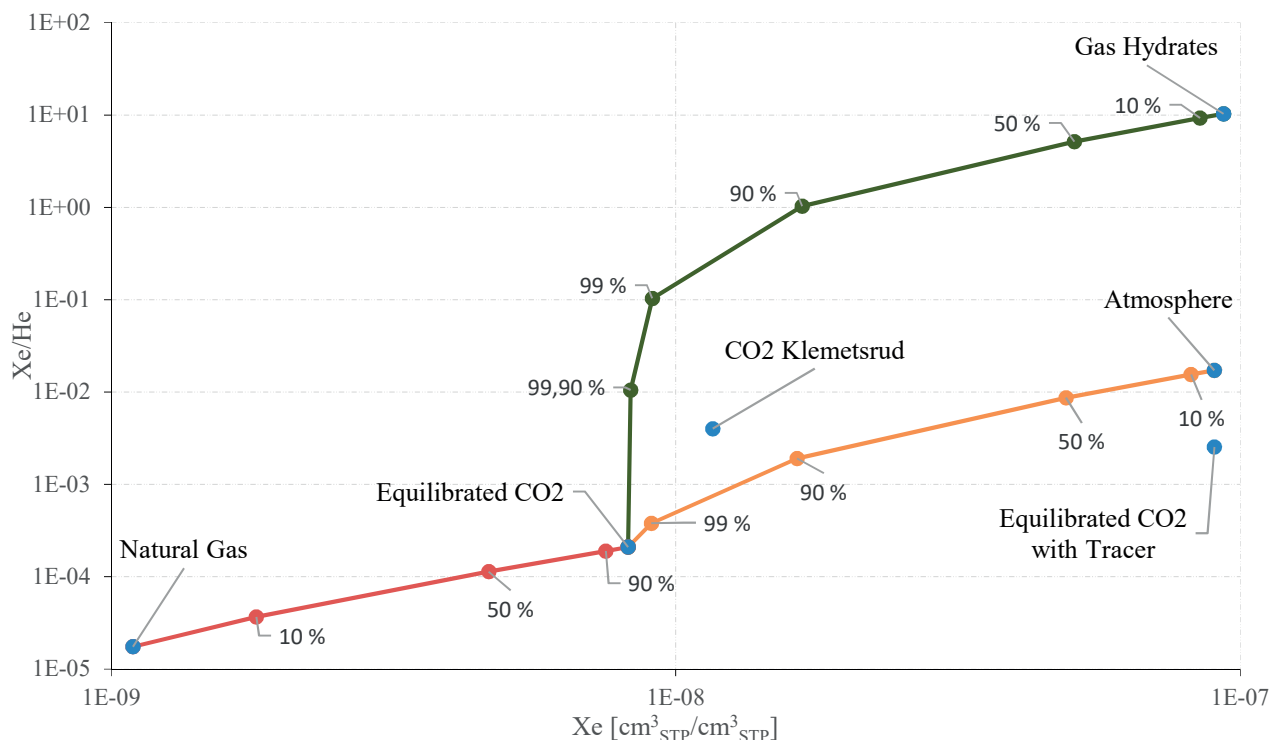


Figure 3: Xe/He vs Xe plotted with mixing lines with equilibrated CO<sub>2</sub> and background fluids (see Sec. 2 and Tab. 1). Mixing lines with the injected, equilibrated CO<sub>2</sub> and signatures of gas hydrates and the atmosphere. Also, equilibrated CO<sub>2</sub> with a tracer addition of 1E-07 cm<sup>3</sup><sub>STP</sub>/cm<sup>3</sup><sub>STP</sub> Xe is included. Mixing lines of injected CO<sub>2</sub> after equilibration with gas hydrates, atmosphere and natural gas with the content of the CO<sub>2</sub> in the mixture in percent.

would further have to account for analytical uncertainty and natural variation of the background fluids. At least the latter one can be addressed by performing a thorough baseline characterization of the storage site prior to injection.

## 5. Conclusion

The derivation of the signature of the injected CO<sub>2</sub> after phase partitioning with the formation water allows to evaluate differentiability of the possible signatures. Comparing the injected CO<sub>2</sub> to other sources depicts the identifiability and attributability of a leakage through noble gases. Here, we have shown examples how a leakage would be detectable and how the volumetric contribution of injected CO<sub>2</sub> can be estimated. Most notably, the difference between the adopted radiogenic signature and that of shallow fluids with atmospheric or other specific signatures, such as gas hydrates, is very pronounced. We also modelled the amounts that would be needed for tracer addition for Kr and Xe. These can be fed into cost calculations for the respective noble gases. This cost can be broken down to a price per ton and set into perspective to the cost of other monitoring measures of a storage project.

However, there are still uncertainties for some of the background fluids even though the shown inferred concentrations from analogues allow to constrain the possible observed concentrations. Thus, we aim to characterize more fluid compositions from oil and gas fields in the North Sea. Further, we aim to analyze sediment samples from the seafloor to characterize shallow signatures. The ICO<sub>2</sub>P project will continue to focus on characterizing the area around the Aurora site,

which has been selected as the storage prospect for the ‘Longship’ project. An extended baseline database will contribute to the goal to conclude on the applicability of noble gas tracers.

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## Appendix B

# Co-Authored Papers

### B.1 In Situ Observation of Helium and Argon Release During Fluid-Pressure-Triggered Rock Deformation

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**Summary** This article presents results from a hydraulic reservoir stimulation experiment conducted in 2017 in the Grimsel Test Site, Switzerland. A seeping fault was sealed off, the water was collected and analysed with the miniRUEDI mass spectrometer. The flow rate was low and the general environment was similar to that faced in Paper IV. The experimental setting therefore served as a foundation for the Mont Terri experiment.

Geodetic and seismic analyses revealed that the applied stimulation treatments led to the formation of new fractures (hydraulic fracturing) and the reactivation of natural fractures (hydraulic shearing). These mechanical alterations (re)-mobilized fluids trapped in the rock mass, that are identified as older fluids due to the enriched He and Ar concentrations.

The results demonstrate that integrating geochemical information with geodetic and seismic data provides critical insights to understanding dynamic changes in fracture network connectivity during reservoir stimulation. The results of this study shed light on the linkages between fluid migration, rock deformation and seismicity at the decameter scale.

The results are also transferable to CO<sub>2</sub> storage reservoirs, considering that fluids within the same rock unit can exhibit very variable noble gas signatures even on small scale. The pressuring could lead to a mixture of differently enriched water masses.







OPEN

# In situ observation of helium and argon release during fluid-pressure-triggered rock deformation

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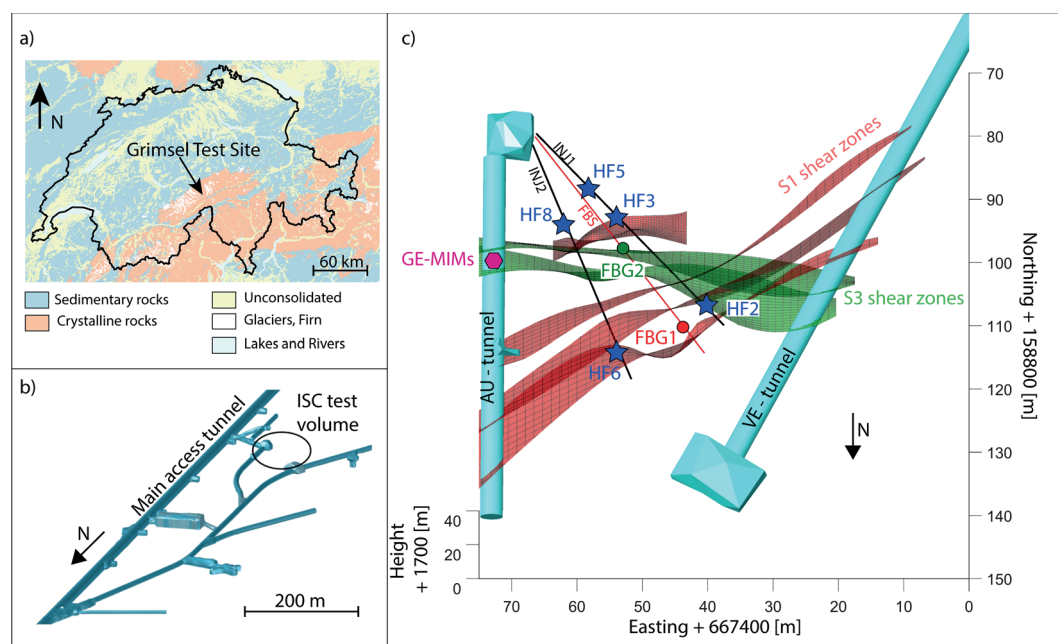
Temporal changes in groundwater chemistry can reveal information about the evolution of flow path connectivity during crustal deformation. Here, we report transient helium and argon concentration anomalies monitored during a series of hydraulic reservoir stimulation experiments measured with an *in situ* gas equilibrium membrane inlet mass spectrometer. Geodetic and seismic analyses revealed that the applied stimulation treatments led to the formation of new fractures (hydraulic fracturing) and the reactivation of natural fractures (hydraulic shearing), both of which remobilized (He, Ar)-enriched fluids trapped in the rock mass. Our results demonstrate that integrating geochemical information with geodetic and seismic data provides critical insights to understanding dynamic changes in fracture network connectivity during reservoir stimulation. The results of this study also shed light on the linkages between fluid migration, rock deformation and seismicity at the decameter scale.

Changes in the crustal stress state caused by natural or human-induced subsurface fluid overpressures can lead to brittle rock mass damage, from the formation of grain-scale microcracks to the failure of kilometric-scale faults<sup>1</sup>. Characterizing the timing and spatial extent of crustal deformation is critical for both industrial applications, including geothermal, oil and gas production, and improving our mechanistic understanding of earthquakes. From this perspective, seismic and geodetic monitoring systems generally provide the vast majority of data collected. Several authors have also proposed that geochemical anomalies may be used as proxies for rock deformation<sup>2–5</sup>.

Fluids in the Earth's crust display highly variable geochemical traits due to the spatial and temporal variability in fluid recharge composition, fluid-rock interactions and residence times. Previous studies have shown extremely variable distributions of residence times, ranging from decades<sup>6</sup> to several hundred or even millions of years for fluids stored in low-permeability rocks<sup>7,8</sup>. In this context, the fluid composition may evolve from diluted waters with modern signatures in recharge areas to saline fluids in the deeper crust, where the fluid composition tends to equilibrate with the host rock mineralogy through dissolution/precipitation processes. By analyzing specific dissolved chemical tracers, one can reconstruct the origin of fluids and gain insights into their recharge, percolation and storage conditions<sup>9,10</sup>.

From this perspective, noble gases such as radon (Rn), helium (He) and argon (Ar) have received particular attention in recent decades because of their widespread occurrence in the subsurface and their low chemical reactivity, proving to be ideal tracers to track the origin of fluids, analyze fluid-rock interactions and determine residence times<sup>7,8,11–14</sup>. Concentrations of dissolved noble gases in subsurface fluids and their isotopic compositions are driven by two main mechanisms: 1) water/air partitioning during recharge, which is sensitive to atmospheric

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**Figure 1.** Overview and location of the experimental test volume for the *In situ* Stimulation and Circulation (ISC) project: (a) geological map of Switzerland (modified from the website <https://map.geo.admin.ch/>, Federal Office of Topography), (b) tunnel network and location of the investigated volume, (c) geological model displaying the main shear zones (modified after Krietsch *et al.*, 2018<sup>23</sup>), along with the main boreholes used for injection (INJ1 and INJ2) and monitoring (FBS), the locations of stimulation (HF#) and strain monitoring (Fiber-Bragg-Grating, FBG) intervals, and the location of the *in situ* gas equilibrium membrane inlet mass spectrometer (GE-MIMS<sup>[24]</sup>) used for monitoring dissolved noble gas concentrations. For a more complete description of the geology of the investigated volume and the monitoring system deployed, readers are referred to Krietsch *et al.*, 2018 and Amann *et al.*, 2018<sup>22,23</sup>.

pressure, temperature and salinity, and 2) radiogenic production in the crust through radioactive alpha-decay of heavy elements (mainly uranium, thorium or potassium) combined with the accumulation of enriched fluids from deeper reservoirs (e.g., the upper mantle)<sup>9</sup>.

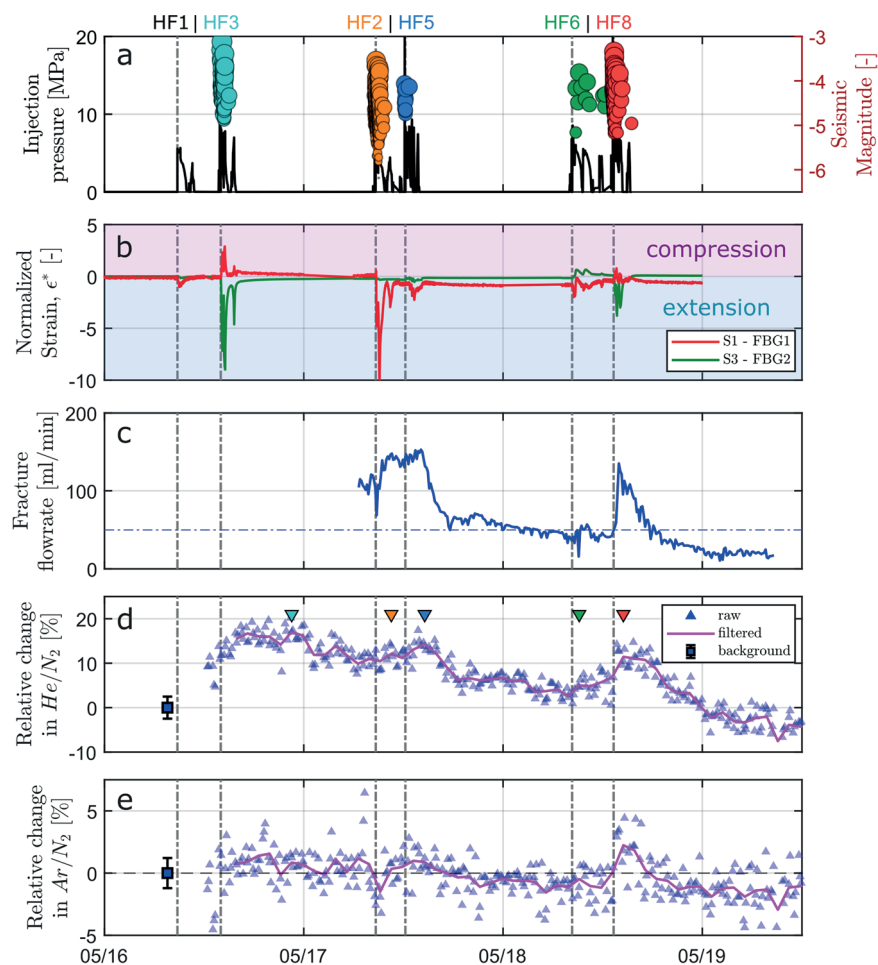
Chemical anomalies created by earthquakes have been explained by the mixing of fluids from different sources (with different chemical compositions) inhibited by changes in flow pathway geometry and hydraulic properties during stress build-up and failure<sup>15,16</sup>. Laboratory studies have also observed the emergence of concentration anomalies in noble gases during rock deformation experiments<sup>17–20</sup>. The authors argued that the progressive increase in microcrack surfaces during increasing stress allows the remobilization of accumulated radiogenic gases and even prior macroscopic failure. While those previous studies suggested that changes in dissolved noble gas concentration could be used as a proxy to track *in situ* stress modifications, field evidence and a description of the mechanisms responsible for fluid remobilization and mixing at the scale of discrete fracture systems are still missing to our knowledge. Our aim in this study is to bridge this knowledge gap through a joint analysis of hydraulic, seismic, deformation and geochemical data gathered during an *in situ* stimulation experiment.

## Experiment description

The study was carried out as part of a series of six controlled hydraulic fracturing (HF) experiments<sup>21</sup> that took place in May 2017 at the Grimsel Test Site, Switzerland (*In situ* Stimulation and Circulation project<sup>22</sup>, [www.grimsel.com](http://www.grimsel.com), Fig. 1). The site consists of a network of tunnels, operated by the Swiss National Cooperative for the Disposal of Radioactive Waste (NAGRA), and these tunnels are located up to 480 m below ground surface in the central Aar granite and granodiorite formations<sup>23</sup>. The stimulated rock volume comprises a relatively intact granodiorite intersected by six subvertical shear zones that can be grouped into 2 sets: ductile shear zones S1 (red in Fig. 1c) and brittle-ductile shear zones S3 (green in Fig. 1c), which form the main transmissive fractured zones<sup>23</sup>.

In this study, we refer to a ‘fracture’ as a single discontinuity that can be identified on optical or acoustic logs (resolution of ~1 mm). A ‘shear zone’ is described as a zone characterized by strong strain concentration that may contain several fractures visible in the optical or acoustic logs. Finally, ‘intact rock’ is understood to be a section of the rock mass with the absence of fractures detectable from the optical and acoustic logs.

From May 16<sup>th</sup> to 19<sup>th</sup>, six high-pressure fluid injections (resulting pressure below 10 MPa during the fracture propagation phase) were performed in two injection boreholes (INJ1–2 in Fig. 1c, labeled HF#) at different depth intervals by isolating 1 m intact rock with double packer systems. A dense network of boreholes was equipped with monitoring systems aimed at capturing hydraulic, strain and seismic responses during stimulation (see Methods). As a complement, a portable gas equilibrium membrane inlet mass spectrometer (GE-MIMS<sup>24</sup>) was installed at a tunnel inflow, where groundwater naturally seeps from an extensional fracture located between the

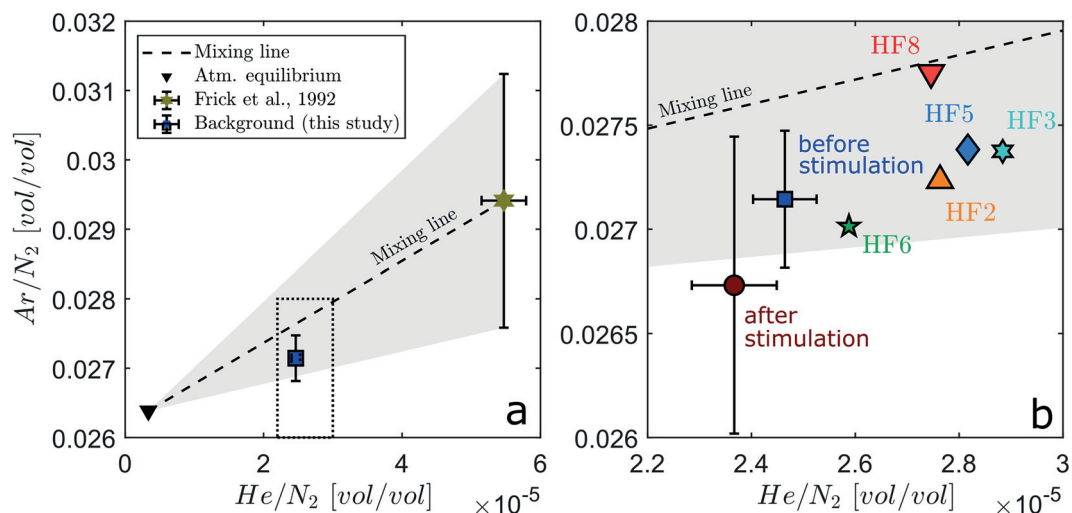


**Figure 2.** Temporal evolution of (a) injection pressure drawn as a continuous black line together with the magnitude of seismic events, which are represented by circle symbols. The diameter of the circles are scaled with the magnitude and the colors differentiate the responses from the different HF experiments; (b) normalized strain  $\epsilon^* = \epsilon/\text{std}(\epsilon)$  [-] for two selected strain sensors located in both S1 and S3 shear zones. Strain has been normalized by its standard deviation to better appreciate the shapes of both time series. Positive values indicate compressional regimes, while negative values indicate extensional regimes; (c) fracture discharge rates monitored at the GE-MIMS station. The horizontal dashed line represents the average discharge rate prior to stimulation; (d) relative changes in He/N<sub>2</sub> from background [%] and (e) relative changes in Ar/N<sub>2</sub> from background [%]. The background average ratio in He/N<sub>2</sub> and Ar/N<sub>2</sub> are shown as blue squares. Background error bars are  $2\sigma$  and represent the typical analytical error. Time series of raw data are shown as blue triangles, and low-pass filtered ratios are represented by magenta lines. The different stimulation experiments are labeled with HF# at the top of the figure. Colored triangles in subpanel c identify the peaks in He/N<sub>2</sub> concentrations following each HF# experiment, which are further analyzed in Fig. 3.

two targeted S3 shear zones. The GE-MIMS allowed monitoring of near-real-time He, N<sub>2</sub>, and Ar concentrations dissolved in the pore water with a sampling interval of 8 minutes (see Methods). We anticipated potential effects of the low flowrates involved at the seeping fracture that could lead to incomplete gas/water equilibration at the extraction membrane of the GE-MIMS, by normalizing the He and Ar concentrations by the concentrations of dissolved N<sub>2</sub> (only of atmospheric origin in the case of this experiment). This ensures that the observed He/N<sub>2</sub> and Ar/N<sub>2</sub> ratios only reflect the variations of dissolved He and Ar in the fluid (see Methods).

## Results

**Strain, seismic and hydraulic responses induced by high-pressure fluid injection.** The evolution of strain monitored in the S1 and S3 shear zones during the different high-pressure injections showed that both extension and compression deformation were involved. (Figure 2b, positive values for the compressional regime and negative values for the extensional regime). Deformation patterns show variability across the different HF experiments with amplitudes ranging from  $-386.3 \mu\epsilon$  extension to  $+28.5 \mu\epsilon$  compression (Table 1SM in Supplementary Material). As a general interpretation of the main processes involved, we argue that while the extensional regime is dominant at the locus of injection due to local increasing pore pressure, the nearby structures experience a compressive response to balance the stress perturbation. As the injection progresses,



**Figure 3.** (a) Ar/N<sub>2</sub> as a function of He/N<sub>2</sub>. The mixing line (short dashed line) from atmospheric (black reversed triangle) to (He, Ar)-enriched fluid end-members (olive star) was collected in 1982 during the realization of exploration boreholes and reported in Frick *et al.*<sup>30,31</sup>. The confidence area for binary mixing is drawn as a gray triangle accounting for the variability in the Ar and N<sub>2</sub> concentrations measured in the samples collected in 1982. The background average ratio and standard deviations are shown as blue squares and error bars. (b) is a zoom of the concentration range of interest (corresponding to the dashed rectangle in panel a) with peak concentrations presented with different symbols and colors for the different HF# experiments (refer to Fig. 2d for the locations of peak concentrations identified in the time series of He/N<sub>2</sub>). Concentrations measured after the stimulation experiment are shown as a wine-colored circle. Error bars are 2σ.

the stress perturbation diffuses away from the stimulation interval, enabling fracture initiation and reactivation. After a peak in deformation is monitored almost simultaneously with the maximum injection pressure, the strain decreases back to values close to the initial background. This recovery is mostly controlled by the combined effect of fluid pressure diffusion within the fracture network and elastic relaxation of the rock. Although the strain signal appears to be mainly dominated by reversible processes, the residual strain observed in the time series indicates that irreversible deformation due to imperfect normal fracture closing is involved<sup>21</sup>.

A total of 774 seismic events were located during the whole experiment, with magnitudes ranging from -6.2 to -3.1 (Fig. 2a). Seismic events strongly correlate with injection activities, and even though similar fluid volumes were injected during all experiments following similar injection protocols, strong variability in seismic characteristics was observed across a single HF experiment (Table 1SM in Supplementary Material) - *i.e.*, located seismic events, maximum induced magnitudes, seismically activated areas (determined with planar seismic cluster geometries) and Gutenberg-Richter *b*-values, as well as seismogenic indices,  $\Sigma$  (determined for experiments exhibiting more than 50 induced events). The Gutenberg-Richter *b*-values and the seismogenic indices,  $\Sigma$ , are of particular interest when comparing the intensity of seismic responses across different tests<sup>25</sup>. Note that a low *b*-value (*i.e.*, comparably larger magnitude events with respect to small magnitude events) and a high seismogenic index (*i.e.*, comparably increased seismogenic reaction to a unit volume of fluid) represents a comparable, more intensive seismic response<sup>26</sup> (Fig. 1SM in Supplementary Material).

High-pressure injection activities promoted increases in discharge rates monitored at the GE-MIMS station during HF2, 5, 6 and 8 (Fig. 2c). These fast reactions at the tunnel outlet reveal efficient connectivity and high hydraulic diffusivities (on the order of 0.1–1 m/s) of the stimulated fracture network.

The main differences in seismic, deformation and hydraulic responses among the HF experiments allow for the definition of two main clusters, which are primarily constrained by their location with respect to the S3 shear zones: (I) HF3, 5 and 8 were all carried out south of the S3 shear zones. All of these experiments showed high injection pressures, fast pressure decay after injections and relatively low fluid recovery. This finding suggests that the stimulated fractures progressively connected to the preexisting transmissive fracture system, allowing the injected fluid to propagate efficiently within the network<sup>21</sup>. HF3 and HF8 induced 70 and 183 micro-seismic events, respectively, for which deformation patterns were mainly dominated by the extensional regime along the S3 shear zones. While HF3 showed a dispersed seismic cloud over a large rock volume, seismic events located during HF8 were organized along a well-identified fracture plane (estimated area of 235 m<sup>2</sup>, see Table 1SM in Supplementary Material) propagating toward the S3 shear zone. The seismic response of experiment HF3 (*b* = 1.55,  $\Sigma$ : -4.8) increased compared to experiment HF8 (*b* = 2.66,  $\Sigma$ : -9.0), and the largest magnitude event of the experiment series was monitored during HF3. HF5 showed the lowest number of seismic events (11), with a smaller seismically activated area (<10 m<sup>2</sup>) and a compressional regime along S3<sup>21,26</sup>. (II) HF2 and 6 were performed within the S1 shear zones - *i.e.*, north of the S3 shear zones. Pressure diffused at a slower rate within the reservoir, and fluid recovery was higher after the shut-in phase, suggesting lower connectivity to the preexisting transmissive network. Extensional deformation along S1 was dominant during HF2, while HF6 was mainly linked to compressional deformation of S1 and the extension of S3<sup>21</sup>. HF6 did not induce a significant

number of microseismic events, which was most likely because the experiment was conducted in an interval that contained preexisting S1 structures that were hydraulically stimulated in a previous experiment series<sup>26</sup>. HF2 promoted the highest number of induced seismic events, an activated surface area of approximately 95 m<sup>2</sup> and the largest seismic response of the HF experiment series<sup>26</sup> ( $b = 1.35$ ,  $\Sigma = -4.0$ , also see Table 1SM and Fig. 1SM in Supplementary Material).

**Geochemical tracing of involved fluid origins before stimulation.** Pore water sampled at the monitoring station shows low mineralization with an electrical conductivity of 300  $\mu\text{S}/\text{cm}$ , a pH of 9 and a temperature of 12 °C (Table 2SM in Supplementary Material). N<sub>2</sub> and Ar concentrations of  $1.4 \cdot 10^{-2}$  ccSTP/g and  $3.7 \cdot 10^{-4}$  ccSTP/g, respectively, indicate that both elements are oversaturated by approximately 25% with respect to atmospheric-equilibrated water. This excess of N<sub>2</sub> and Ar is typically assigned to an “excess-air” phenomenon, which implies oversaturation in gas species due to the partial dissolution of entrapped air bubbles during recharge<sup>27,28</sup>. Ar shows 2.5% more oversaturation than N<sub>2</sub>, while He is also significantly enriched with respect to atmospheric-equilibrated water of approximately 800% ( $3.4 \cdot 10^{-7}$  ccSTP/g, Table 2SM in Supplementary Material). This oversaturation in He, combined with the slight enrichment in Ar over N<sub>2</sub> of ~2.5%, shows the accumulation of radiogenic-produced noble gases, which is confirmed by a low <sup>3</sup>He/<sup>4</sup>He ratio of the excess He (taking a value of  $2.2 \cdot 10^{-7}$ , which is 6.1 times lower than the atmospheric ratio<sup>29</sup> of  $1.384 \cdot 10^{-6}$ ; please refer to Table 2SM in the Supplementary Material and Methods).

Even larger excesses in He, Ar and N<sub>2</sub> (*i.e.*, concentrations exceeding the expected atmospheric equilibrium concentrations) were also determined in pore waters collected during early sampling campaigns on exploration boreholes in 1982<sup>30,31</sup> (Fig. 3a and Table 2SM in Supplementary Material). These differences indicate that the initial pore water sampled in 1982 could have slightly different meteoric origins with higher soil temperatures at recharge, different residence times controlled by local geological heterogeneity, or that the present-day concentrations may be diluted by modern fluids injected during recent activities performed in the tunnel, *i.e.*, extensive drilling, hydraulic testing, and *in situ* experiments. Nevertheless, the relationship between He/N<sub>2</sub> and Ar/N<sub>2</sub> (Fig. 3a) is remarkably aligned along a mixing line between the non-atmospheric fluid enriched in He and Ar that was collected in 1982 and modern air-equilibrated meteoric water. Note that the background concentration (Fig. 3a) plots in the mixing triangle (in gray on Fig. 3) defined by the variability in Ar/N<sub>2</sub> ratios measured in the pore water sampled in 1982. This confirms that binary mixing between the two geochemical end-members explains the fluid composition seeping from the fracture where the GE-MIMS was installed. It also allows us to estimate that the (He, Ar)-enriched end-member contributes approximately 25% to the background fluid composition.

**Geochemical anomalies involved during reservoir stimulation.** The first two injections, HF1 and HF3, performed on May 16<sup>th</sup> (Fig. 2) caused a significant increase in He/N<sub>2</sub> ratios of up to 17% relative to the background values, while Ar/N<sub>2</sub> ratios remained close to background values (Fig. 2d,e). After this sudden increase, the He/N<sub>2</sub> ratios tend to continuously decrease. This trend was interrupted by enhanced ratios in response to the following stimulation (HF2, 5, 6 and 8). Experiments HF3 and 8, which were carried out south of the transmissive shear zones and the closest to the GE-MIMS monitoring station (24 and 17.4 m geometrical distance from locus of injection, respectively, Table 1SM in Supplementary Material), were associated with an abrupt increase in the He/N<sub>2</sub> anomalies. HF5 fostered a much smaller anomaly, while HF2 and HF6 were hardly detectable against the given experimental uncertainty of the dissolved gas analysis. In response to HF8, an ~2% increase in the Ar/N<sub>2</sub> ratio was observed.

Enhanced He/N<sub>2</sub> ratios correlate with the occurrence of microseismic events (Fig. 2a) and increase in discharge rates (Fig. 2c), indicating that He-enriched fluids are remobilized within the fracture network during the injection cycles. The majority of normalized peak concentrations lines up subparallel to a binary mixing line of the two respective end-members and within the confidence area (Fig. 3b), suggesting that no other type of fluid is involved. Mixing fractions of the He/N<sub>2</sub> and Ar/N<sub>2</sub>-enriched fluid ranged from 20 to 45%, whereby maximum values were linked to stimulation experiments HF3 (33%), HF5 (33%) and HF8 (45%), while HF2 and HF6 showed lower values of 28% and 21%, respectively. It is remarkable that these two sets of experiments identified based on the differences in geochemical anomalies match the two clusters that have been previously identified as having similar hydromechanical responses. Experiments HF3, 5 and 8, which were performed south of the S3 shear zone, have enabled the development of new fractures that effectively connected the preexisting transmissive fracture network and were followed by higher He/N<sub>2</sub> anomalies. However, experiments HF2 and HF6, which were undertaken north of the S3 shear zone, induced poor fracture connection with the transmissive S3 shear zone and were followed by lower He/N<sub>2</sub> anomalies.

The day after the last experiment, He/N<sub>2</sub> and Ar/N<sub>2</sub> reached a lower level than before the experiments, with a contribution of approximately 11.5% from the (He, Ar)-enriched fluid. Figure 3b also shows that the concentrations plot outside the confidence area for binary mixing. This difference may result from the modifications in the fracture network connectivity due to the stimulation, which tends to increase the contribution of a different source of water that was not previously identified (*i.e.*, meteoric water recharged under different temperature and pressure conditions).

## Discussion

**He and Ar concentration anomalies provide insights into new flow pathways formed in response to reservoir stimulation.** Our assessment demonstrates the ability of GE-MIMS technology to monitor fluid remobilization in response to *in situ* rock deformation. The temporal scales of the processes involved not only require a high-frequency monitoring system<sup>24,32</sup> but also a multi-tracer approach, *i.e.*, He, Ar and N<sub>2</sub> in the case of the GTS. Complementing the findings of previous experiments performed in the laboratory<sup>17–20</sup>, as

well as those advanced from large-scale observations in the context of earthquakes<sup>5</sup>, we interpret these anomalies as the release of radiogenic He (and Ar) stored in the rock mass that could be transported within the newly created and pre-existing fracture system. While the identification of the source of the mobilized fluids is still speculative, two complementing hypotheses on its origin are proposed: (1) radiogenic He (and Ar) accumulated in the rock matrix is released by the formation of new fracture areas; and/or (2) the shearing of pre-existing fractures induces the remobilization of stagnant fluids, with higher residence times enriched in radiogenic He and Ar, trapped in lower transmissivity zones of the fracture network. In both scenarios, the improved connectivity resulting from the stimulation, combined with the high pore pressure gradients involved, allows the transport and dispersion of those fluids with their respective noble gas signature away from their original location.

The magnitude and temporal scaling of the produced concentration anomalies depend not only on concentration contrasts between the involved fluids (geochemical end members) but also on flow connectivity and transport properties of the fracture system through which the fluids move. The time lag between the high-pressure injection and the peak in noble gas concentrations may provide estimates of the average fluid velocities involved if the original location of the activated fluids is known, *i.e.*, assuming that most of the (He, Ar)-enriched fluid originates from the vicinity of the injection point where the fractures are created or reactivated. In the case of this experiment, advective velocities of  $10^{-3}$  to  $10^{-2}$  m/s can explain the observed time lags. The rate at which concentration anomalies dissipate within the fracture network may provide information on how much the fluid is dispersed within the reservoir, with the dispersion length scaling with the square root of the residence time<sup>33</sup>. We observed a He/N<sub>2</sub> restitution rate during HF3 that suggested higher dispersion than for the other experiments, with an anomaly that persisted during the whole week of the experiment. HF3 also showed a dispersed seismic response, suggesting the activation of multiple fractures in the surrounding volume, enhancing the dispersion of (He, Ar)-enriched fluids. In contrast, the abrupt and sharp He/N<sub>2</sub> anomaly linked to HF8 relaxes to the corresponding background values within 10 hrs. Since HF8 was performed closest to the GE-MIMs and induced the creation of a single fracture plane that rapidly connected to the transmissive S3 shear zone<sup>21,26</sup>, the dispersion of (He, Ar)-enriched fluids is expected to be lower than in the case of HF3.

## Conclusion

In this paper, we provide *in situ* evidence of He and Ar anomalies occurring during the deformation of a crystalline fractured system at the decameter scale. We observed clear differences in the magnitude and temporal dynamics of these anomalies for different clusters of stimulation experiments that displayed differences in their hydro-seismo-mechanical responses. Complementing previous hypotheses drawn from laboratory experiments, we speculate that the remobilization of (He, Ar)-enriched fluids is principally controlled by (1) the extent of the deformed rock mass and the area of the ruptured fractures, which may control the amount of (He, Ar)-enriched fluids released; (2) the type of deformation, which may lead to different concentration anomalies. The generation of a single fracture plane in intact rocks leads to a stronger (He, Ar) signal, typically experiment HF8, than in the case of the reactivation of multiple fractures that may disperse the signal, typically experiment HF3; (3) the efficiency of the newly generated fracture of connecting with the preexisting transmissive fracture system, allowing its transport within the reservoir; and (4) the distance of the source of (He, Ar)-enriched fluids from the monitoring point.

Overall, high-frequency noble gas measurements in fractured rocks may help to improve the conceptualization of the nature and evolution of flow paths in response to stimulation operations, and complement the information obtained from hydraulic, deformation and seismic monitoring systems. Specifically, the analysis of the magnitude and temporal scaling of hydrogeochemical changes, such as the described noble gas anomalies, may inform about the evolution of the hydraulic connectivity and the transport properties of the stimulated fracture network, which is information that is not accessible through classic seismic and geodetic methods.

From similar perspectives, valuable information could be gained through high-frequency noble gas monitoring in both CO<sub>2</sub> injection and oil and gas extraction projects, where undesired gas migration pathways toward shallower aquifers could be identified during operation<sup>34,35</sup>. Monitoring noble gas concentrations may also help understand the impact of natural seismic events on regional aquifer connectivity, providing critical information to link seismicity to fluid migration in the Earth's crust.

## Methods

**Injection protocol.** Six high-pressure fluid injections were performed in two injection boreholes (INJ1-2 in Fig. 1, labeled HF#) by isolating 1 m of intact rock with double packer systems. The targeted injection intervals had a constant base length of 1 m. Prior to each HF test, the interval integrity and proper packer sealing were tested with a short pulse test. HF tests started with a flow rate-controlled (5 l/min) injection cycle that lasted for 30 seconds to initiate fracturing (*i.e.*, formation breakdown), followed by shut-in and bleed-off phases. Subsequently, the fracture was propagated with flow rate-controlled injections (up to 100 l/min). A total of 1,000 liters of fluid was injected during each test over all cycles. Each injection cycle was followed by a shut-in phase. During HF5, HF6 and HF8, water and a rheology modifier (mixture with xanthan gum polymer) were used to achieve a viscosity-dominated propagation regime<sup>21</sup>. The latter consists of a xanthan-salt-water mixture providing 35 times higher viscosity than water. For the tests undertaken with xanthan-salt-water, a supplementary flushing cycle was performed to flush as much xanthan as possible out of the fracture. The last cycle was a pressure-controlled step test to evaluate the post-stimulation injectivity of the created hydraulic fracture and to estimate the stress acting normal to the hydraulic fracture (jacking pressure). Note that HF1 is not considered in this study because it suffered from logistical issues that prevent any reliable monitoring and interpretation.

**Deformation monitoring.** To obtain quantitative information about the deformation field inside the test volume, three boreholes (referred to as FBS boreholes in Fig. 1) were drilled, and each borehole was equipped

with 20 Fiber-Bragg-Grating strain sensors. The sensors provide one-dimensional borehole-parallel information about local deformations. Prior to installation, fractures were mapped along the borehole from optical and acoustic televiewer logs<sup>36</sup>. Care was taken to ensure that the strain sensors covered the different geological features of interest, i.e., including preexisting fractures, shear zones and intact rock sections. The sensors have a length of 1 m, accuracy of 1 microstrain, and resolution of 0.1 microstrain and were measured at a sampling rate of 1000 Hz. The strain signals described in this paper (from borehole FBS1 at 22.35 m and 42.2 m depths) each cover one of the main shear zones (S3.1 and S1.3) targeted by the stimulations, providing information about the extent of deformation and its temporal variability.

**Seismic monitoring.** Seismicity was monitored during the injection<sup>26</sup>, shut-in and bleed-off phases of the six HF experiments using 26 highly sensitive piezoelectric acoustic emission sensors. Eight of the acoustic emission sensors were deployed in four monitoring boreholes in proximity to the injection intervals. Seismicity was recorded continuously at a sampling rate of 200 kHz. Seismic event detection was performed using a standard recursive short-time-average/long-time-average coincidence trigger, whereby picking was carried out manually. Seismic event location was performed in an anisotropic, homogeneous velocity model. An amplitude-based magnitude  $M_A$  was estimated for located seismic events and corrected for angle-dependent sensitivity variations and coupling quality of acoustic emission sensors. The amplitude-based magnitudes  $M_A$  were finally adjusted to absolute magnitudes  $M_W$  determined for a subset of larger magnitude seismic events. The absolute magnitudes  $M_W$  were estimated from acoustic emission sensors installed in nearby tunnels that were collocated with calibrated accelerometers. The collocation of acoustic emission sensors and accelerometers allowed for a cross-calibration of the acoustic emission sensors. Finally, to determine absolute magnitudes  $M_W$ , the theoretical displacement source spectrum introduced by Boatwright (1978)<sup>37</sup> was fitted to the recorded displacement spectrum on the cross-calibrated acoustic emission sensors<sup>26</sup>.

**Continuous noble gas monitoring.** A portable gas equilibrium membrane inlet mass spectrometer (GE-MIMS, Gasometrix GmbH) was installed at a nearby natural seeping zone related to the transmissive S3 shear zones (Fig. 1c). The instrument allows for near-real-time on-site environmental quantification of partial pressures and hence the concentrations of gases dissolved in water<sup>24</sup>. The fluid was collected from the whole area of the seeping shear zone. The fracture was sealed with a plastic foil and waterproof mortar, forcing the fluid to drain by gravity to the GE-MIMS. The sealing was designed to avoid any secondary gas exchange with the atmospheric gases. Background monitoring with GE-MIMS revealed anoxic conditions, confirming that the sampling system was airtight. Then, the collected water was transferred to GE-MIMS membrane contactors (two parallel Micro Modules 3 M Liqui-Cel MM-0.5–1 × 1 Series), which are specifically designed for low flow rates (from 5–1000 ml/min). Water temperature and total gas pressure in the membranes' gas head space are determined by the respective sensors. The small head space further maintains a high temporal resolution at the respective water flow rate. He, Ne (in dry gas), Ar, Kr, N<sub>2</sub>, and O<sub>2</sub> were analyzed every 8 min with an analytical uncertainty of 1–3%. Gas standards from an air-filled Plastigas bag were analyzed every 40 min to calibrate the sample data. Natural background gas concentrations were measured for two days prior to the start of stimulation activities, from May 12<sup>th</sup> to May 14<sup>th</sup> (Fig. 2).

The flow rate of the seeping pore water was measured at the outflow of the membrane contactors using a tipping bucket flow gauge connected to a Siemens micrologger starting on May 17 at 6 am before the initiation of HF2. The monitored seeping fracture provided flow rates ranging from 20 to 160 mL/min. These flow rates are lower than the recommended value for air-equilibrated water to maintain the mass balance of the gases in the membrane contactor at gas/water<sup>24</sup>, implying that the partial pressures of the different gas species in the head-space could be controlled by diffusion-limited gas/water exchange across the membranes themselves. This would lead to incomplete gas/water equilibration, especially during periods of low water flow. To avoid any potential effects arising from incomplete gas/water equilibrium within the membrane contactor, we normalized the noble gas concentrations by the measured concentrations of dissolved N<sub>2</sub>, which is only of atmospheric origin in our case study. With ratios of aqueous diffusion coefficients of 3.34 (He/N<sub>2</sub>) and 1.06 (Ar/N<sub>2</sub>), diffusive fractionation would result in an excessive He/N<sub>2</sub> ratio compared with Ar/N<sub>2</sub> if the mass balance of the gases in the membrane contactors would be limited by diffusion across the membrane. However, the reverse was observed in the dataset, which indicates that the observed He/N<sub>2</sub> and Ar/N<sub>2</sub> ratios are not fractionated by non-equilibrium effects in the membrane contactors, most likely due to the higher gas concentrations in the fluid compared to air-equilibrated water. Therefore, the observed He/N<sub>2</sub> and Ar/N<sub>2</sub> ratios accurately reflect the ratios of dissolved He, Ar and N<sub>2</sub> in the fluid.

The concentrations of He and Ne, as well as the <sup>3</sup>He/<sup>4</sup>He ratios of individual water samples obtained in standard copper tubes, were analyzed at the noble gas laboratory at ETHZ according to standard analytical protocols. For technical details, the reader is referred to the work of Beyerle *et al.*<sup>38</sup>.

### Data availability

The Grimsel ISC Experiment Description is available at <https://doi.org/10.3929/ethz-b-000310581>. Data used in this publication are available from the ETH Zürich research collection. Partial pressures and discharge rates measured at the GE-MIMS station can be found at <https://doi.org/10.3929/ethz-b-000365199>. The seismic dataset, as well as hydraulic data of the Grimsel ISC hydraulic fracturing experiments, are available at <https://doi.org/10.3929/ethz-b-000276170> and the hydromechanical dataset is available at <https://doi.org/10.3929/ethz-b-000328270>.

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### Author contributions

C.R. and R.K. initiated this research; J.D., V.G., F.A., and B.V. initiated the *in situ* stimulation and circulation (ISC) experiment; C.R., R.K., U.W. and M.B. developed the geochemical monitoring setup; U.W. and C.R. installed the GE-MIMS and collected samples; J.D., V.G., F.A., M.K. and B.V. designed the hydraulic, deformation and seismic monitoring setup; N.D., M.J., J.D., V.G., F.A., and B.V. designed and conducted the hydraulic fracturing experiment; C.R., U.W., M.B. and R.K. processed and interpreted the geochemical data; H.K. and N.D. processed and interpreted the deformation data; L.V. processed and interpreted the seismic data; N.D., B.B., M.J. and M.K. processed and interpreted the hydraulic data; C.R., N.D., U.W., B.B., H.K. and J.D. interpreted the overall dataset; H.K. created Figure 1; C.R. and U.W. created Figures 2 and 3; L.V. created Figure 1SM; C.R., U.W., B.B., N.D., H.K. and L.V. wrote the initial manuscript; and all coauthors reviewed the manuscript.

### Competing interests

The authors declare no competing interests.

### Additional information

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## Appendix C

# Conference Participations

During the course of this PhD the scientific exchange on conferences has played a key role in fostering the progress of the work. Here, conference participations are listed.

### 2021

- **Goldschmidt 2021** Geochemical monitoring of a CO<sub>2</sub> injection into a caprock analogue. U.W. Weber, A.P. Rinaldi, C. Roques, A. Zappone, S. Bernasconi, M. Jaggi, Q. Wenning, S. Schefer, M. Brennwald, R. Kipfer. Online,
- **Trondheim CCS Conference, TCCS-11** On the distinctiveness of noble gases in injected CO<sub>2</sub> from background fluids. U. W. Weber, N. Kampman, A. Sundal. Online, 2021-06-21 - 2021-06-23
- **14th International Conference on Greenhouse Gas Control Technologies, GHGT-15** Noble Gases as Monitoring Tracers in CCS: A Case Study with CO<sub>2</sub> from the Waste-to-Energy Plant Klemetsrud, Norway U.W. Weber, N. Kampman, T. Mikoviny, J. Thomassen, A. Sundal. Online, 2021-03-15 - 2021-03-18
- **ICO<sub>2</sub>P Seminar** Applicability of noble gas tracers in Norwegian CO<sub>2</sub> capture and storage schemes. U.W. Weber, A. Sundal. 2021-03-09

### 2020

- **Goldschmidt 2020** Experiences from the ICO<sub>2</sub>P Project applied to Migration Monitoring of Injected CO<sub>2</sub>. U.W. Weber, Ulrich Wolfgang; Sundal, Anja; Hellevang, Helge; Kipfer, Rolf. Online, 2020-06-21 - 2020-06-26
- **EGU General Assembly 2020** Tracer Design and Gas Monitoring of a CO<sub>2</sub> Injection Experiment at the ECCSEL CO<sub>2</sub> Field Lab, Svelvik, Norway. Weber, Ulrich Wolfgang; Heeschen, Katja; Zimmer, Martin; Rphaug, Martin Hagen; Hagby, Klaus Falk; Ringstad, Cathrine; Sundal, Anja. Online, 2020-05-04 - 2020-05-08
- **EGU General Assembly 2020** Fault hydromechanical characterization and CO<sub>2</sub>-saturated water injection at the CS-D experiment (Mont Terri Rock Laboratory). Wenning, Q. C., Rinaldi, A. P., Zappone, A., Grab, M.,

## C. Conference Participations

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Roques, C., Weber, U. W., Jaggi, M., Bernasconi, S. M., Guglielmi, Y., Brennwald, M., Kipfer, R., Madonna, C., Obermann, A., Nussbaum, C., and Wiemer, S.: Online, 2021-05-04 - 2021-05-08

- **The 34th Nordic Geological Winter Meeting** Gas Composition of the Svelvik Ridge Aquifers Used to Design Noble Gas Tracers for a CO<sub>2</sub> Injection Experiment. Weber, Ulrich Wolfgang; Røphaug, Martin Hagen; Revheim, Maiken; Sundal, Anja. Oslo, 2020-01-08 - 2020-01-10
- **The 34th Nordic Geological Winter Meeting** Tidal effect on pressure in upper and lower aquifer of the Svelvik Ridge. Revheim, Maiken Kristiansen; Weber, Ulrich Wolfgang; Hagby, Klaus Falk; Ringstad, Cathrine; Sundal, Anja. Oslo, 2020-01-08 - 2020-01-10
- **The 34th Nordic Geological Winter Meeting** Hydrogeological characterization of Holocene deposits in the Svelvik aquifer – implications for reservoir properties. Sundal, Anja; Weber, Ulrich Wolfgang; Kürschner, Wolfgang; Grimstad, Alv Arne; Ruden, Fridtjof; Aagaard, Per; Hagby, Klaus Falk; Revheim, Maiken Kristiansen; Ringstad, Cathrine. Oslo, 2020-01-08 - 2020-01-10

## 2019

- **Trondheim CCS Conference TCCS-10** Noble Gases as Monitoring Tracers: Sampling Campaigns at Capture Sites Technology Center Mongstad and Melkøya. Weber, Ulrich Wolfgang; Kipfer, Rolf; Brennwald, Matthias S.; Ringrose, Philip; Sundal, Anja. Trondheim, 2019-06-17 - 2019-06-19
- **MiniRuedi Seminar** Quantification of Air-Water Gas Exchange with the miniRUEDI. Weber, Ulrich Wolfgang; Brennwald, Matthias; Kipfer, Rolf. Dübendorf, 2019-03-04 - 2019-03-05
- **MiniRuedi Seminar** Temporal Variation in Noble Gas Signatures of Captured CO<sub>2</sub>. Weber, Ulrich Wolfgang; Sundal, Anja; Brennwald, Matthias; Kipfer, Rolf. Dübendorf, 2019-03-04 - 2019-03-05
- **CLIMIT PhD and PostDoc seminar** Weber, Ulrich Wolfgang; Sundal, Anja. Application of noble gas signatures in monitoring schemes for offshore CO<sub>2</sub> storage (ICO<sub>2</sub>P). Oslo, 2019-01-18
- **Vinterkonferansen 2019** Noble Gas Release during Reservoir Stimulation. Weber, Ulrich Wolfgang; Roques, Clement; Kipfer, Rolf; Dutler, Nathan; Krietsch, Hannes; Jalali, Reza; Gischig, Valentin; Doetsch, Joseph; Valley, Benoit; Amann, Florian. Bergen, 2019-01-07 - 2019-01-09

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## 2018

- **14th International Conference on Greenhouse Gas Control Technologies, GHGT-14** Monitoring real time, in-line variations of noble gas concentrations during CO<sub>2</sub> capture operations by means of a portable mass spectrometer. Sundal, Anja; Weber, Ulrich Wolfgang; Brennwald, Matthias; Ringrose, Philip; Enaasen Flø, Nina; Johnsen, Kim; Leila, Faramarzi; Aagaard, Per; Kipfer, Rolf. Melbourne, 2018-10-21 - 2018-10-25
- **Goldschmidt 2018** CO<sub>2</sub> Capture Processes Monitored with Noble Gas Measurements. Weber, Ulrich Wolfgang; Sundal, Anja; Brennwald, Matthias; Ringrose, Philip; Aagaard, Per; Kipfer, Rolf. Boston, 2018-08-12 - 2018-08-17