



# Risks attributable to water quality changes in shallow potable aquifers from geological carbon sequestration leakage into sediments of variable carbonate content



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## ABSTRACT

The consequences of CO<sub>2</sub> leakage from geological sequestration into shallow aquifers must be fully understood before such geo-engineering technology can be implemented. A series of CO<sub>2</sub> exposure batch reactor experiments were conducted utilizing 8 sediments of varying composition obtained from across Denmark including; siliceous, carbonate and clay materials. Sediments were exposed to CO<sub>2</sub> and hydro-geochemical effects were observed in order to improve general understanding of trace metal mobility, quantify carbonate influence, assess risks attributable to fresh water resources from a potential leak and aid monitoring measurement and verification (MMV) program design. Results demonstrate control of water chemistry by sediment mineralogy and most significantly carbonate content, for which a potential semi-logarithmic relationship with pH and alkalinity was observed. In addition, control of water chemistry by calcite equilibrium was inferred for sediments containing >2% total inorganic carbon (TIC), whereby pH minima and alkalinity maxima of approximately 6 and 20 mequiv./l respectively were observed. Carbonate dominated (i.e. >2% TIC) and mixed (i.e. clay containing) sediments showed the most severe changes in water chemistry with large increases in all major and trace elements coupled to minimal reductions in pH due to high buffering capacity. Silicate dominated sediments exhibited small changes in dissolved major ion concentrations and the greatest reductions in pH, therefore displaying the greatest propensity for mobilization of high toxicity pH sensitive trace species.

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## 1. Introduction

Initially employed to increase oil recovery from hydrocarbon reservoirs or to avoid carbon emissions tax (Kongsjorden et al., 1997; Blunt et al., 1993), implementation of carbon capture and geological sequestration (CCS) as a greenhouse gas mitigation technique has slowly progressed over the past 10 years. Consequently several demonstration projects have been conducted (Hovorka et al., 2011), are operating (Kirste et al., 2010) or are in planning (BSCSP, in press) and one full scale project is underway (QUEST, 2013). During permitting of such CCS projects it must usually be proven beyond any reasonable doubt that potential storage sites will not leak and pose a risk to overlaying potable drinking water supplies. Nonetheless, it is essential the consequences of leakage are fully understood in order to design effective MMV programs and to assess the potential risks posed to shallow groundwater in the unlikely event of leakage occurring. Consequently a variety of studies have been published in recent years attempting to

characterize potential water chemistry changes likely induced by leakage. The majority of published studies describe numerical modeling exercises (Zheng et al., 2013; Carroll et al., 2009; Vong et al., 2011; Zheng et al., 2009, 2012; Wilkin et al., 2010; Jaffe and Wang, 2003; Navarre-Sitchler et al., 2013), whilst fewer report laboratory studies (Little and Jackson, 2010; Lu et al., 2010). In addition an increasing number of field based investigations are also being reported (Kharaka et al., 2010; Trautz et al., 2013; Peter et al., 2012; Cahill and Jakobsen, 2013) which are essential in order to ultimately determine the effects of leakage on groundwater quality. The studies published so far have increased our understanding regarding risks posed by leakage and begun to characterize the changes in water chemistry likely to occur. Hydro-chemical effects of leakage in several different hydro-geological settings and the physico-chemical mechanisms by which they manifest have been explored (i.e. mineral dissolution and exchange/surface processes). Overall, the literature has shown clearly that effects of CO<sub>2</sub> leakage are wholly site specific with the specific sedimentary composition of an overlaying strata exerting ultimate control on geochemical change (Keating et al., 2010; Newmark et al., 2010; Siirila et al., 2012). This makes it difficult to generalize potential chemistry evolution in an aquifer during leakage without site specific

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laboratory or field testing. Unfortunately studies currently published do not cover all geological or hydro-geochemical settings potentially impacted by leakage. Nor do they fully characterize, quantify or prove conclusively the geochemical mechanisms occurring following CO<sub>2</sub> exposure. For this reason it is essential further experiments are conducted which attain direct measurements of hydro-chemical change following exposure of previously un-studied shallow aquifer sediments to CO<sub>2</sub>. Furthermore, it is essential the chemical processes induced by CO<sub>2</sub> exposure are more comprehensively characterized and quantified. Subsequently fundamental processes should be identified and generalizations potentially made allowing risks to water resources from CO<sub>2</sub> leakage to be more generally assessed, at least to some degree. This study describes such further simple CO<sub>2</sub> exposure batch experiments conducted on 8 sediments from across Denmark including siliceous sands, chalks and clays. The aim of the study is to further characterize the processes controlling water chemistry change, assess risks posed to groundwater quality and identify implications for MMV programs across a range of sediment types. By conducting a comprehensive suite of analysis (i.e. sediment composition determination, inorganic carbon content determination, total element determination using hydrofluoric acid abstraction, BET surface area measurements and basic geochemical speciation modeling using PHREEQC (Parkhurst and Appelo, 2013)) the study aims to determine and quantify elemental release in comparison to mineralogy and in particular carbonate content. This study is the first of its kind, to the authors' knowledge, to address quantitatively carbonate content in a CCS context, explore a geology dominated by glaciations (i.e. the geology of Denmark) and address the effects of CO<sub>2</sub> on shallow aquitard (i.e. clay/till) material and chalk. The results complement existing published results by concurrence of some common trends, observation of new trends and also development of ideas and concepts regarding the geochemical effects of CO<sub>2</sub> in shallow potable aquifers.

## 2. Methods

Eight sediment samples were selected from the borehole archives of the Geological Survey of Denmark and Greenland (GEUS), representative of groundwater related aquifer and aquitard sediments in Denmark. Sediments were characterized as follows; % total (by weight) composition (XRD Philips Powder Diffractometer model PW-1050/25 equipped with a Control Unit PW-1710), inorganic carbon content (combustion and IR detection), surface area (BET method) and total elemental composition (hydrofluoric acid digestion and ICP-MS analysis). The sediments studied including mineralogy are described in Table 1. The sediments were studied in two phases, both to ensure the methodology and sampling regime was adequate and for logistical reasons. In phase 1; calcareous glacial sand (cgs), non-calcareous glacial sand (ncgs), till and eem (a clay like material deposited in the Eemian interglacial period characterized by high levels of mollusk shell) were studied. Following phase 1, phase 2 sediments; calcareous post-glacial sand (cps), non-calcareous post-glacial sand (ncps), bryozoan chalk (bc) and chalk (c) were studied. Bryozoan chalk is characterized by extremely high calcite content (100% in this case) and usually small amounts of clay deposited under shallow conditions, while the chalk contains a small amount of quartz (2%) and is a generally deposited under deeper conditions. In this case the two chalk sediments are also seen to have different surface areas and thus may show differences in reactivity. Samples were obtained dry from storage and disaggregated by hand or pestle and mortar (depending on consolidation), thinly spread and allowed to further dry at room temperature for 72 h. Sediments were weighed into 50 g portions in duplicate, placed inside a 300 ml glass flask, capped with a rubber

sealed septum with 200 ml of de-ionized water and equilibrated for a seven day period. This should allow a reasonably stable baseline water chemistry to be attained as observed in similar experiments performed using de-ionised water (Lu et al., 2010). In the study by Lu et al. (2010) a stable background chemistry was observed after 6 days equilibration for a range mixed composition sediments (silicate and carbonate), thus the method was deemed acceptable to allow a focus on the effects of CO<sub>2</sub> exposure. After the equilibration period of 7 days, background samples (20 ml removed by syringe) were taken with pH (Hach Lange probe, accuracy 0.2) and alkalinity (gran titration method) determined immediately and trace metal concentrations determined by ICP-OES analysis (Varian Vista MPX. Detection limits in electronic appendix) following preservation (filtration with 0.45 µm acetate filters and acidification with 10%, w/w HNO<sub>3</sub>). Following the initial background sample, batch reactors were immediately exposed to food grade CO<sub>2</sub> for 30 min via a needle injection and venting system. CO<sub>2</sub> was injected directly into the liquid and sediment mixture causing turbulent mixing at an over-pressure of approximately 1.2 bars. Two venting needles allowed excess gas to escape after passing through the liquid into the head space with an overpressure maintained for 30 min. After cessation of the gas injection the over-pressure was allowed to equalize for approximately 5 s before the venting needles were removed leaving the bottles sealed with a CO<sub>2</sub> reservoir of 1 bar partial pressure in the head space. Samples were then taken over 3 days and analyzed for pH, alkalinity and major cations/trace metals as described for the background samples. Following the 3 day initial period, phase 1 sediments were exposed to a further 30 min CO<sub>2</sub> interval twice more whilst phase 2 sediments were exposed once. Samples were then taken from phase 1 and phase 2 sediments for a further 23 and 3 days respectively. Additional de-ionized water was also added to all sediments after the initial 3 day period to ensure sufficient volume for further sampling. Geochemical speciation calculations were conducted using PHREEQC (Appelo and Parkhurst, 1998) modeling code and statistical analysis (i.e. correlation) determined using MYSTAT statistical calculation program.

## 3. Results

### 3.1. Physico-chemistry

Injection of CO<sub>2</sub> induced a rapid change in the carbonate system over the first 72 h as shown in Fig. 1. CO<sub>2</sub> dissolved into each reactors sediment-water mixture inducing slight over-saturation, implying the partial pressure of CO<sub>2</sub> (P<sub>CO<sub>2</sub></sub>) calculated by PHREEQC was slightly above 1 atm within 30 min. Subsequently P<sub>CO<sub>2</sub></sub> stabilized around saturation (i.e. SI=0) for all reactors indicating the injection system effectively dissolved CO<sub>2</sub> in the water phase. Expectedly the CO<sub>2</sub> injection resulted in immediate lowering of pH, increased alkalinity and induction of water-sediment reactions based on the particular mineral composition. Carbonate containing sediments (see Table 1.) observed an average increase in alkalinity of approximately 18.26 mequiv./l in contrast to 1.17 mequiv./l observed in non-calcareous sediments from pre- to post-CO<sub>2</sub> exposure levels. Concurrently carbonate and non-carbonate containing sediments observed average decreases in pH of 1.03 and 1.94 units. Following the initial decrease in pH a slight rebound was observed for all sediments over the proceeding 72 h.

### 3.2. Major and minor elements

Graphs of major and minor cation concentration development during the first 72 h for all sediments are shown in Fig. 2. For all sediments Ca, Mg, Mn, Ni, Sr, Ba, Na and K concentrations all showed a sudden increase post CO<sub>2</sub> exposure followed by stabilization at

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