

# Geochemical characterization of Rupel (Boom) Clay material: pore water composition, reactive minerals and cation exchange capacity

**OPERA-PU-UTR521** 

Title:

Geochemical characterization of Rupel (Boom) clay material: pore water composition, reactive minerals and cation exchange capacity

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Date of publication: May 2015

Keywords reactive minerals, in-situ pore water, cation exchange capacity, sequential extraction Specialist area: geochemistry, mineralogy, analytical chemistry

# Summary

Prediction of the speciation of radionuclides in Boom Clay pore water and their retardation by interactions with Boom Clay require knowledge about the composition of Boom Clay pore water, the inventory of reactive solids and understanding of interactions between Boom Clay and pore water. Boom Clay material was obtained from undisturbed cores collected at the province of Zeeland and from drill cuttings retrieved from a drilling in the province of Limburg. Solid phase characterization included determination of carbon, nitrogen and sulphur contents, measurement of cation exchange capacity (CEC) and sequential extraction of iron phases. These analyses complement the geochemical characterization of Boom Clay samples from the Netherlands documented in the report OPERA-PU-5-2-1-TNO-1. Pore water was obtained by mechanical squeezing of Boom Clay material from Zeeland and has been analysed. Additionally, dilution experiments were performed in which the clay material was suspended with demineralized water or a 0.1 M NaHCO<sub>3</sub> solution. In the latter experiments, the solution composition was monitored over a period of 30 days. The main focus of this study lies on comparing pore water and solid phase composition at the two locations in the Netherlands to those reported for Boom Clay in Belgium which has been extensively investigated and reported in various SCK-CEN reports.

In comparison with Boom Clay in Belgium and in Limburg, Boom Clay in Zeeland has generally lower contents in carbonates, pyrite, and organic carbon. The measured CEC values at both locations in the Netherlands vary between 7 and 35 meq/100g and are, for most samples, in the range reported for Boom Clay in Belgium (7-30 meq/100g). The CEC of Boom Clay in Zeeland tends to be higher than the CEC of samples from Limburg. Iron bound to silicates is the largest iron fraction in all samples and pyrite is generally the largest pool of reactive iron in samples from Limburg while, in Boom Clay from Zeeland, the amount of HCl extractable Fe(III) is often of comparable size as the amount of Fe in pyrite. Samples from Boom Clay in Zeeland have higher contents of iron (hydr)oxides compared to samples from Limburg.

In contrast to the pore water in Belgian Boom Clay, which has a fresh water characteristic, pore water collected from the location in Zeeland has a strong seawater signature with chloride concentrations corresponding to 70-96 % of chloride concentrations in seawater. The pore waters have, in general, a deficit of marine cations ( $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ) while  $Ca^{2+}$  concentrations exceed those of seawater. In some samples, sulphate is highly enriched, while sulphate is depleted in others. The pH is lower than in seawater and in some samples acidic pH values around 3.0 were measured. The time evolution of the solution compositions in the dilution experiments is often not exhibited by all experiments with the same material. The change in compositions does often not depend systematically on solid to solution ratio or whether bicarbonate or demineralized water was used. When calcium carbonates are present in the solid, concentrations of cations, in particular of calcium, increase in experiments with demineralized water while calcium carbonate solution is used. In most samples, sulphate is removed from solution during the experiment. One sample from a core top, which has been obviously affected by drying and oxidation, showed very deviating behaviour during the dilution experiments.

Intrusion of seawater ions into Boom Clay at Zeeland is a dominant process controlling the major ion composition in the pore water. The cation assemblage is modified by exchange processes with adsorbed ions. Oxidation of pyrite and Fe(II) is another important process affecting pore water and solid phase composition. Indications are given that oxidation occurred in the pore water after sampling and in the cores during storage. However, it is also possible that oxidation is ongoing insitu or could have taken place in the past. It could be, that oxidation has occurred contemporaneously during partial erosion of Boom Clay in Zeeland before deposition of the Breda Formation. In particular, the relative low concentrations of pyrite, organic carbon and calcite in the Boom Clay in Zeeland can be an indicator for an oxidation event. Dissolution of pyrite can be coupled to the dissolution of calcium carbonates and lead to concomitant increase of dissolved sulphate and calcium, which, in turn, can eventually result in precipitation of gypsum. Potential for removal of dissolved sulphate reduction. However, further research is required to identify the underlying process and to evaluate whether the process also occurs in-situ.

### Samenvatting

De speciatie van radionucliden in het poriewater van de Boomse Klei en hun retardatie door interacties met de Boomse klei zijn belangerijke factoren in ondezoek naar eindberging van radioactief afval. Om de radionuclidespeciatie en retardatie te voorspellen is er kennis nodig over de samenstelling van het poriewater van de Boomse Klei, de reactieve vaste stoffen in de Boomse klei en het is belangrijk te begrijpen wat de interacties tussen de Boomse Klei en het poriewater zijn. Boomse kleimateriaal was verkregen van onverstroorde kernen uit Zeeland en van boorgruis uit een boorgat in Limburg. Voor het karakteriseren van de vaste fase van de Boomse Klei zijn koolstof, stikstof, en zwavelgehaltes gemeten, de kationenuitwisselingscapaciteit (CEC) bepaald en een sequentiele ijzerextractie uitgevoerd. Deze analyses zijn een aanvulling op de geochemische karakterisatie van Nederlandse Boomse Kleimonsters die in het OPERA-PU-5-2-1-TNO-1 rapport beschreven is. Poriewater, verkregen uit mechanisch geperste Boomse Kleimonsters uit Zeeland, was tevens geanalyseerd. Daarnaast is ook een verdunningsexperiment uitgevoerd waarbij de klei in verschillende verhoudingen gesuspendeerd werd in gedeminereraliseerd water, of in een 0.1 M NaHCO<sub>3</sub> oplossing. In deze experimenten werd de compositie van de oplossing gemonitord over een periode van 30 dagen. De focus van dit onderzoek ligt op het vergelijken van de samenstelling van het poriewater en de vaste stof van de Boomse Klei van de twee Nederlandse locaties, met die van de Boomse Klei in Belgie, welke uitgebreid onderzocht en vermeld zijn in verscheidene SCK-CEN rapporten.

In vergelijking met de Boomse Klei uit België en Limburg heeft de Zeelandse Boomse Klei over het algemeen een lager carbonaat-, pyriet- en organisch materiaalgehalte. De gemeten CEC-waarden liggen voor beide Nederlandse locaties tussen de 7 en 35 meq/100g, en vallen meestal binnen de gemeten CEC-waarden van de Belgische Boomse Klei (7-30 meq/100g). De CEC van de Boomse kleimonsters uit Zeeland neigen naar iets hogere waarden dan die uit Limburg. Uit de ijzerextractie blijkt dat, in alle Boomse Kleimonsters, ijzer gebonden aan silicaten de grootste fractie van het totale ijzergehalte uitmaakt. Pyriet is de grootste fractie van reactieve ijzer in Limburg, terwijl in Zeeland de hoeveelheid HCI-extraheerbare Fe(III) vaak ongeveer gelijk is aan die van pyriet. Boomse Kleimonsters uit Zeeland bevatten hogere ijzer(hyrdr)oxidegehaltes in vergelijking met de Limburgse monsters.

In tegenstelling tot het zoetwaterkarakter van het Belgische Boomse Klei-poriewater, heeft poriewater geëxtraheerd uit de Zeelandse Boomse Klei chlorideconcentraties van 70-96% van de chlorideconcentraties in zeewater. Het poriewater heeft, over het algemeen, een tekort aan mariene kationen (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>), behalve  $Ca^{2+}$  dat juist boven de zeewaterconcentraties ligt. Sommige poriewatermonsters hebben sulfaatconcentraties boven die van zeewater, in anderen zijn sulfaat concentraties lager. De pH is lager dan dat van zeewater en in sommige monsters werden zuurgraden van rond de pH 3.0 gemeten. De tijdsevolutie van de verschillende ionconcentraties in het verdunningsexperiment is bij experimenten met hetzelfde materiaal vaak niet gelijk. De verandering van de samenstelling hangt niet systematisch samen met de verschillende verdunningsverhoudingen, of het feit dat bicarbonaat of demi-water gebruikt was. Als klei monsters, die calciumcarbonaten bevatten, met gedemineraliseerd water verdund worden zorgt oplossen van calciumcarbonaten voor een toename van de kation-concentraties, vooral die van Ca2+. Als verdunningsexperimenten met hetzelfde materiaal, maar met bicarbonaat oplossing, uitgevoerd worden vertoont de oplossing geen veranderingen als gevolg van calciumcarbonaat. In het merendeel van de experimenten, waarbij in het begin sulfaat in de oplossing is verschenen, is het aan het eind van de verdunningsexperimenten weer verdwenen. Een monster van de top van een van de kernen, die duidelijke sporen van oxidatie en uitdroging had, vertoonde afwijkende resultaten in vergelijking met de andere verdunningsexperimenten met andere monsters.

Een belangrijk proces dat de ionsamenstelling in het Boomse Klei-poriewater in Zeeland bepaalt, zijn intrusies van zeewaterionen in de Boomse Klei. De kationsamenstelling verandert door uitwisselingsprocessen met geadsorbeerde ionen. Oxidatie van pyriet en Fe(II) is een ander prominent proces dat het poriewater en de vaste fase kan beïnvloeden. Er zijn indicaties dat er oxidatie Fe(II) of pyriet heeft plaatsgevonden in het poriewater nadat het verkregen werd en in de kernen tijdens opslag. Het is echter ook mogelijk dat de oxidatie zich in-situ afspeelt of in het verleden heeft plaatsgevonden. Vroegere in-situ oxidatie zou eventueel voorgekomen kunnen zijn bij de gedeeltelijke erosie van de Boomse Klei in Zeeland voor de afzetting van de Formatie van Breda. Specifiek de relatief lage concentraties pyriet, organische koolstof en calciet in de Boomse

Klei in Zeeland zijn indicatoren dat oxidatie heeft plaatsgevonden. Het oplossen van pyriet kan worden gekoppeld aan het oplossen van calciumcarbonaat wat leidt tot een bijbehorende toename van opgelost sulfaat en calcium, die op hun beurt zouden kunnen precipiteren in de vorm van gips. Verdwijning van opgelost sulfaat door interactie met Boomse Klei, gedetecteerd in de verdunningsexperimenten, kan eventueel ook veroorzaakt zijn door microbiële sulfaatreductie. Echter, meer onderzoek is nodig om de onderliggende processen te identificeren en om te beoordelen of deze ook in-situ plaatsvinden.

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## 1. Introduction

#### 1.1.Background

This report complements the mineralogical and geochemical characterization of the Boom Clay in the Netherlands which is presented in report OPERA-PU-5-2-1-TNO-1 (Koenen and Griffioen, 2014). The latter report focuses on the characterization of samples which were collected from the TNO core house in Zeist. These cores were stored without specific precautions to prevent alterations due to oxidation by atmospheric oxygen or desiccation. These two processes might change the composition and mineralogy of the material. Possible reactions include the oxidation of organic matter or of redox-sensitive solids such as pyrite  $(FeS_2)$  or siderite  $(FeCO_3)$ . The oxidation of pyrite can lead to the formation of Fe(III) (hydr)oxides and the generation of sulphuric acid, which in turn, can further react with carbonates and eventually result, for example, in the precipitation of gypsum (CaSO<sub>4</sub>) or jarosite. Indications for secondary gypsum formation were obtained from the inspection of Boom Clay material from the TNO core house. Dissolved ions can form precipitates upon the evaporation of water, while the amount of dissolved ions can be altered during the concentration process due to the interactions with the solid phase including ion-exchange and other sorption processes. Hence, material from these cores is only suitable for the determination of parameters which are not or only marginally susceptible to alteration upon oxidation and drying. These parameters include the mineralogy of less reactive minerals (e.g. silicates), total element content, or particle size. For the determination of reactive solid phases or the analysis of pore water composition, fresh or carefully preserved cores are required.

Here, we characterize Boom Clay material from two different locations in the Netherlands. The investigated material was either obtained from cores which were stored in wax sealed stainless steel cylinders or from core cuttings which were preserved against drying and oxidation directly after collection. Note, the Boom Formation according to the Belgium nomenclature is equivalent to the part of the Rupel Clay Member which overlies the upper part of the sandy Vessem Member of the Rupel Formation according the nomenclature in the Netherlands. As the term Boom Clay is well introduced in the international community concerned with the geological disposal of radioactive waste, the term Boom Clay will be used when referring to the part of the Rupel Clay Member which corresponds to the Boom Formation in Belgium.

Characterization and quantification of reactive solids phases in the geological formation hosting radioactive repositories is a prerequisite for assessing the interaction of radionuclides with the host rock. The group of reactive solids is not a well-defined category. In general, the group comprises solids which have large specific surface areas and react fast enough with the pore water so that they contribute significantly to controlling its composition. The involved reactions include dissolution, precipitation, and transformation of solids as well as interfacial processes such as adsorption. For reactive solids, the time scale of these heterogeneous reactions are often considerably shorter than the residence time of the pore water in the system. In this case, the reactions between solids and pore water constituents can be appropriately described by using an equilibrium approach. In contrast, a kinetic approach is usually required for describing reactions involving less reactive solids such as, for example, the weathering of primary silicates.

An equilibrium model was used to reproduce the compositions of pore waters retrieved from MORPHEUS piezometers in Mol, Belgium (De Craen et al., 2004). In this model, the CO<sub>2</sub> pressure and the sulphate concentration was constrained and the solution was equilibrated with the cation exchange complex and following minerals: chalcedony, kaolinite, calcite, siderite and pyrite. was also fixed. This model includes several of the reactive solids which have been reported in Boom Clay and which are listed in Table 1.1 (De Craen et al., 2004). Other mineralogical components with lower reactivity are quartz, K-feldspars, albite, and heavy minerals such as ilmenite, rutile, anatase, xenotime, monazite or zircon. Another important group of reactive solids, which are particularly relevant in soils, are metal (hydr-)oxides such as aluminium or iron (hydr-)oxides. However, the presence of any of these solids in Boom Clay have not been reported so far.

Group	Minerals
clay minerals	illite, smectite, illite/smectite ML, kaolinite chlorite, chlorite/smectite
	ML, glauconite
carbonates	calcite, siderite, dolomite, ankerite
sulphides	pyrite
phosphates	apatite
organic carbon	

Table 1.1. Reactive solids detected in Boom Clay (De Craen et al., 2004)

The capability of reactive solids to effect pore water composition implies that they can also exert influence on radionuclide migration. Various interactions between solids and solution can contribute to the retardation of radionuclide transport by, for example, adsorption, co-precipitation (structural incorporation), or redox transformations. In addition to these direct interactions with radionuclides, the reactive solids can control the concentration of other pore water constituents which, in turn, can affect the speciation of radionuclides in solution and their interaction with solids. One example is the buffering of pH and adjusting the dissolved inorganic carbon level by dissolution or precipitation of carbonates. Hence, determining the in situ pore water composition and understanding the interactions between pore water and Boom Clay is required to predict the speciation of dissolved radionuclides and to identify and characterize reactions which control the phase distribution of radionuclides.

#### 1.2.*Objectives*

Great efforts have been taken to determine the in situ pore water composition of Boom Clay and to geochemically characterize unaltered Boom clay material from several locations in Belgium. Unaltered material has been retrieved at locations where Boom Clay outcrops or during the construction and operation of the HADES research facility. The findings are presented in a series of SCK-CEN reports and publications and lead to following main conclusions (see: Honty and De Craen, 2012):

- the mineralogical and geochemical properties of the Boom Clay are rather constant throughout the deposit.
- due to the layered structure the composition varies vertically but the corresponding layers can be followed at a regional scale.
- statistical analysis reveals that, on a vertical scale, the composition of Boom Clay pore water is related to the originating layer for some of the investigated layers. However, when influence of saline water is absent (e.g. in Mol) the composition does not show pronounced vertical variations.
- On an East-West transect, Boom Clay pore water in the west of Belgium (Essen) is influenced by saline water, possibly originating from the underlying aquifer (De Craen et al., 2006).

According to our knowledge, well preserved Boom Clay material from the Netherlands has not been geochemically characterized so far. Hence the question arises whether the trends regarding the presence of reactive solids and pore water composition, as observed in Belgium, extend towards the deeper part of the basin in the Netherlands. In view of pore water composition, salinities up to 24 g/L have been reported from Boom Clay at a location in Zeeland (Rijkers et al., 1998). These high salinities were attributed to an influence of water from the Scheldt estuary. This suggest that the influence of marine water on the Boom Clay pore water in the Netherlands can be larger than in Belgium.

The goal of this report is to investigate presence and quantity of reactive constituents and related parameters such as cation exchange capacity of Boom Clay material from the Netherlands. Furthermore, attempts are made to retrieve pore water and to reconstruct the in-situ pore water composition. The results are compared with those obtained from unaltered material in Belgium in order to evaluate possible regional differences and to identify processes which have caused these differences.

# 2. Sampling location and sample treatment

#### 2.1. Sampling location

Boom Clay material was obtained from two locations in the Netherlands: cores were collected from a series of drillings in the province of Zeeland (Fig. 2.1) and core cuttings were retrieved from a geothermal drilling in Grubbenvorst, located in the south of the Netherlands (Drilling CAL-GT-02). The selection of material was based on its availability and Boom Clay at these locations might not be representative for Boom Clay, which is deposited in deeper parts of the basin and which is presently situated in a depth interval being relevant for radioactive waste deposition.

At the location in Zeeland, the Boom Clay strike-line runs approximately from NW towards SE and is dipping towards SW (Fig. 2.2). In the different drillings in Zeeland, Boom Clay is found between 63 m and 80 m elevation. The thickness of the Boom Clay in the drillings varies between approximately 10 m and 18 m. According to the digital geological model, the basis of the Boom Clay proceeds evenly along the striking and dipping lines, while the morphology of the upper boundary is undulating. The Breda Formation is part of the Upper North Sea Group, which overlies disconformably or unconformably the Lower North Sea Group (TNO, 2003). The Boom Clay is the top layer of the Lower North Sea Group at the location in Zeeland. Hence, the variation and thickness and the undulating boundary between Boom Clay and the Breda Formation can be a consequence of partial erosion of the Boom Clay before the Breda Formation was deposited. At Grubbenvorst, Boom Clay has a thickness of about 100 m extending over an depth interval from about 530 m until 630 m. For this study, samples from three core sections collected from three different drillings in Zeeland are investigated. From the drilling in Grubbenvorst, samples were collected at a depth interval of 5 m.



Figure 2.1: Satellite pictures extracted from Google Map indicating the location of the drillings at the location in Zeeland.





Figure 2.2: Transect exported from the digital geological model of the Netherlands DGM v.1.3. RU= Rupel Formation, TO = Tongeren Formation, BR = Breda Formation, OO = Oosterhout Formation. Other shown formations are Quaternary sediments.

Drilling	Description	Depth section
101	Fat clay with sand (20%), medium plasticity, strong HCl reaction	72.36 - 72.87 m
103A	Fat clay with sand (5%), high plasticity, weak HCl reaction	78.72 - 79.25 m
104	Fat clay with sand (5%), high plasticity, weak HCl reaction, mottled.	75.36 - 75.91 m

Table 2.1. List of core sections used in this study

#### 2.2. Sample treatment

The cores from Zeeland were collected in June 2011 and undisturbed cores were preserved in Shelby tubes which were sealed with paraffin wax at the top and bottom. Remaining void space was filled with clean sand and the tubes were closed with a plastic cap wrapped with PVC tape. For subsampling the core, the steel cylinder was cut on both sides with an angular grinder. The core was removed and transferred into a glove box with  $N_2/H_2$  95%/5% atmosphere. When removed from the Shelby tubes, the surfaces of the cores were covered with a thin brown layer indicating that iron (hydr)oxides had formed upon the reaction with atmospheric oxygen. These layers were removed prior to cutting and subsampling. The core was subsequently sliced in 2 cm thick horizontal layers numbered from top to bottom. The slices were individually installed in PP/Al/PE bags which were heat-sealed inside the glove box and stored at 4 °C until usage.

The structure of the material in the core was not homogeneous. Clay-rich layers with high plasticity alternated with layers with brittle structure and lower clay content. The coloration of this brittle sections varied between white, grey to dark brown. The occurrence of brownish patches in the interior of the core indicate that this material has been affected by oxidation. Oxidation could have happened during storage by oxygen which has been able to intrude the core through larger pores or fractures. Larger pores might have been present in sections with lower content of fine material. Clay-rich parts exhibited a grey colour and did not show indications for oxidation inside the core based on visual inspection.

In order to account for the diversity of structure and composition, slices were selected based on visual inspection which are representative for different core features encountered during slicing (Tab. 2.2). Material from the slices presented in Tab. 2.3 were used in the dilution experiments and subjected to geochemical characterization. The geochemical characterization also included aliquots of other slices and four samples from Grubbenvorst (South-NL).

Core cuttings were retrieved in August 2012 and were captured from the outflow at the drilling rig using a sieve. The cuttings were rinsed with demineralized water to remove drilling fluids and put into PE bags. The PE bags were stored in a glass jar which contained Anaerocult® A bags to remove oxygen and to prevent reaction with atmospheric oxygen during transport into the laboratory. In the laboratory, the samples were transferred inside the glove box into PP/Al/PE bags which were heat-sealed inside the glove box stored at 4  $^{\circ}$ C until usage

Table 2.2. Slices from the different core sections used in this study and the corresponding depth. The number behind the hyphen in the name of the Zeeland samples indicates the number of the 2 cm slices sampled from top to bottom.

Sample Name	Depth (m)
101-14	72.64
101-24	72.84
103A-01	78.72
103A-19a	79.10
103A-19b	79.10
103A-22	79.16
104-10	75.56
104-24	75.76
South-NL 2	525
South-NL 9	570
South-NL 5	595
South-NL 19	620

Table 2.3. Pictures and description of core slices used for dilution experiments and solid phase characterization. The number behind the hyphen in the name indicates the number of the 2 cm slices sampled from top to bottom.



Description

101-14

Grey colour, brittle, low plasticity

#### 103A-01

Top layer of core sample 103A. Grey and brown colours, fractured, most likely effected by dehydration and oxidation during storage.

#### 103A-19a

White to grey colours, brittle, higher content of coarse material (right side on picture)

103A-19b

Grey colour, high plasticity (left side on picture)

103A-22

Grey colour, high plasticity.



Figure 2.3: Pictures illustrating the oxidation of the core at the outer surface (upper left), and the diversity of material showing aggregates of brown colour inside coarser parts of the core (upper right and lower left), and grey colours in sections with high plasticity (lower right).

## 3. Methods

#### 3.1. Pore water collection by mechanical squeezing

Pore water was collected by mechanical squeezing of Boom Clay material. The required sample preparation and the squeezing of the sample was performed at SCK-CEN in Mol, Belgium according to the method described by (De Craen et al., 2004). About 700 g of Boom Clay material was installed inside a steel cylinder which was closed at the top with a piston. The installation of the sample was performed inside a glove box under nitrogen atmosphere to prevent exposure of the sample to atmospheric oxygen. A porous steel plate at the bottom of the cylinder allowed pore water to leave the cylinder when a pressure of 30 MPa was applied to compress the sample. The pressure was applied over one week meanwhile pore water was collected. The pore water left the cylinder through a steel capillary and was collected in a serum bottle which was sealed and equipped with an water filled airlock to allow escape of nitrogen from the bottle and to prevent intrusion of atmospheric oxygen. For the extraction of the first two samples, the flask was closed with a straight, grey butyl stopper. Chemical analysis of the retrieved solution indicate that dissolved Fe(II), S(-II) or nanoparticulate iron sulfides could have entered the bottle and subsequently could have reacted with oxygen. It was assumed that some oxygen could have leaked through the stopper. For this reason, a thick black rubber stopper was used during the third extraction. The squeezing of about 700 g clay material yielded about 40-50 mL of pore water. Afterwards, the remaining water content of the clay was determined by measuring the weight loss of the sample upon drying at 105 °C.

#### **3.2.** *Dilution experiments*

An alternative approach to assess the in-situ composition of the pore water is to suspend clay-rich sediments in demineralized water or bicarbonate solution (De Craen et al., 2004). Two strategies can be followed to obtain information about the in situ pore water composition by dilution experiments: 1) After suspending the clay, an aliquot of the liquid phase is separated as soon as possible from the suspension. If the duration of suspending the material and the subsequent separation of the solution is significantly shorter than the time scale of heterogeneous reactions in the suspension, the composition of the solution reflects, in a first instance, the dilution of the in situ pore water. 2) The contact time of the solution with the clay material is sufficiently long to reach equilibrium. When assuming that the in situ pore water is in equilibrium with the solid phase, the composition of the equilibrated diluted solution resembles the composition of the in situ pore water. In practice, neither of these two idealized situations is usually fulfilled. This is because some heterogeneous reactions occur very fast, such as adsorption, desorption or evasion of gases while others proceed so slowly that equilibrium cannot be reached during a laboratory experiment at room temperature. These slow processes include dissolution or precipitation of minerals or redox transformations. Hence, the composition of the retrieved solutions after dilution have to be carefully interpreted when assessing the in situ pore water composition.

Some constituents of the solution are not very susceptible to heterogeneous reactions such as halide ions. This is because they are not volatile, they do not have a strong tendency to adsorb to mineral surfaces and their concentration is usually not controlled by solids with fast dissolution or precipitation kinetics. The concentrations of other constituents such as alkaline earth metal ions are very likely to be effected by water-mineral interactions, even when the diluted solution is extracted rapidly. The cation composition in the solution can be altered even during a short contact time because cation exchange reactions have time scales of seconds and minutes. In order to obtain information about the potential role of mineral- water interactions in controlling the composition of the extracted solution after dilution, experiments were performed in three different solid to solution ratios and solution was retrieved after four different time intervals.

When the solution composition is solely controlled by dilution of the in-situ pore water, the composition of the latter can be determined based on the dependency of the concentrations (C) in the diluted solutions on the ratio of the volume added solution to the mass of clay material ( $V_{added}$  /  $m_{solid}$ ):

$$[\mathbf{3.1}] \qquad \frac{1}{C} = \frac{V_{pore}}{n_{pore}} + \frac{m_{solid}}{n_{pore}} * \frac{V_{added}}{m_{solid}}$$

 $V_{pore}$  is the volume of in situ pore water and  $n_{pore}$  is the total amount of the constituent initially present in the in-situ pore water. When dilution is the dominant factor controlling the solution composition, the reciprocal value of the concentration depends linearly on the volume of the added solution. The slope of the line, obtained by linear regression analysis, gives the reciprocal value of the initial amount of the constituent in the pore water. The concentration of the constituent in the pore water can be directly obtained from the intercept of the regression line with the y-axis. However, the uncertainty of the intercept is typically large. For this reason, the concentration of the pore water was calculated based on the amount of the compound in the pore water, obtained from slope of the regression line, and the pore water volume. The latter was determined independently from the weight loss upon freeze-drying. Pore water concentrations were only reported from the dilution method when the coefficient of determination,  $r^2$ , was larger than 0.95.

For the dilution experiments, Boom Clay material was ground and homogenized inside the glove box, added into 50 mL PP centrifuge tubes and mixed with 0.1 M NaHCO<sub>3</sub> solution or demineralized water. Prior to addition, the pH of the NaHCO<sub>3</sub> solution was adjusted to 8.12. This solution is in equilibrium with a CO<sub>2</sub> pressure of  $10^{-2.4}$  atm, which has been reported for Boom Clay in Mol, Belgium (De Craen et al., 2004) The preparation of the suspensions and the collection of samples were performed in a glove box with a N<sub>2</sub>/H<sub>2</sub> 95%/5% atmosphere. After the preparation of the suspensions, the centrifuge tubes were installed in a glass jar with a rubber sealing ring as an additional protection against the intrusion of atmospheric oxygen. The glass jars were then removed from the glove box and placed on a temperature controlled horizontal shaker, on which the suspensions were constantly agitated at 26 °C. All dilution experiments were performed in duplicate.

solution ratios.		
Solid to solution ratio	Amount clay sample	Volume solution
[g /L]	[g]	[mL]
25	1.25	50
50	2.50	50
200	8.00	40

Table 2.4 Composition of the different dilution experiments and the corresponding solid to solution ratios.

For sampling the solution, the glass jars were transferred back into the glove box and an aliquot of the suspension was removed and added into a 15 mL PP centrifuge tube. The remaining suspension was returned into the glass jar and placed back on the shaker. The pH was determined in the aliquots and 0.5 ml of the suspension was kept for TXRF analysis. The remaining aliquots were centrifuged for one hour at 2700 g. After transferring back into the glove box, the supernatant was carefully decanted and filtered through a 0.2  $\mu$ m pore size, nylon membrane, syringe filter. One ml of the filtered solution was acidified with 100  $\mu$ l 0.2% HNO<sub>3</sub> for ICP-OES analysis, and the remaining solution was kept for other analyses.

#### **3.3.** Sequential extractions

Several schemes have been proposed to determine the concentrations of reactive Fe containing minerals in sediments or soils. Here, the sequential extraction was carried out according to the modified procedure developed by (Claff et al., 2010) (Table 2.5). Per 1 g of sample, 40 mL of the extraction solution was added. The sequential extraction were performed in triplicate. The first three time steps were carried out inside a glove box under a  $N_2/H_2$  atmosphere. The last three steps were performed outside the glove box.

Extraction Step	Extractant	Phase extracted	References
1	1 M Magnesium chloride (MgCl <sub>2</sub> ) at pH 7, extracted for 1 hour	Exchangeable fraction of adsorbed Fe and readily soluble Fe- salts.	(Tessier, 1979)
2	1 M Hydrochloric acid (HCl), extracted for 4 hours	Carbonates and other minerals sensitive to low pH.	(Larner, 2006; Scouller, 2006)
3	0.1 M Sodium pyrophosphate, pH 10.4 $(Na_4P_2O_7)$ , extracted for 16 hours.	Iron bound to organic matter.	(Donisa, 2007)
4	Sodium citrate/dithionite solution buffered to a pH of 7.5 with NaHCO <sub>3</sub> (CDB), extracted for 15 minutes in a water bath of 75 °C.	Crystalline iron oxides	(Gleyzes, 2002)
5	Concentrated nitric acid (HNO <sub>3</sub> ), extracted for 2 hours	Pyrite	(Huerta Diaz, 1990)
6	Aqua regia	Residual fraction of solid bound Fe	(Mossop, 2003)

For the aqua regia extraction, the sediment samples were dried overnight in an oven of 75 °C after being transferred into Teflon® reaction vessels. After drying, 1.5 mL of concentrated HNO<sub>3</sub> and 4.5 mL of concentrated HCl (aqua regia) was added to the sample and reacted at 90°C overnight within the closed vessels. The following day, the vessels were opened and fluids were evaporated at 160 °C. After evaporation, 20 mL of 2% HNO<sub>3</sub> was added to the dried residuals and reacted 12 h at 90 °C. Afterwards, the remaining amount of 2% HNO<sub>3</sub> was determined by weighing and the solution was analyzed with ICP-OES. Additional, an aqua regia extraction was performed with Boom Clay material which has not undergone the previous extraction steps. As a quality indicator, the sum of the extracted Fe during the various steps should be similar to the Fe recovered in the independent aqua regia extraction.

Between the steps of the sequential extraction, the samples were centrifuged at 2800 g for 10 minutes. The supernatant was decanted into a 50 ml Greiner tube and acidified with 2% HNO<sub>3</sub> prior to ICP-OES analyses. After the concentrated HNO<sub>3</sub> step, the solution was diluted with demineralized water. Between the extraction steps 1, 2, 3 and 5, the solids were resuspended with MgCl<sub>2</sub>, centrifuged again at 2700 g for 1 h, and the washing solution was decanted. MgCl<sub>2</sub> solution was used instead of demineralized water as otherwise clay particles remained in suspension after centrifugation. After step 4, the sediment was rinsed with CDB solution. All the extraction steps were carried out at room temperature, except for step 4, which was carried out in a water bath of 75 °C, and aqua regia extraction was performed at 90 °C.

#### **3.4.** *Cation exchange capacity*

Two different methods were used to determine the cation exchange capacity (CEC): the Ag-thiourea method (Dohrmann, 2006) and the Cu [Trien] method (Honty, 2010; Ammann, 2005). Due to problems related to the precipitation of elemental Ag during the application of the Ag-thiourea method, only results from using the Cu [Trien] method are reported.

The Cu[Trien] solution was prepared by dissolving 1.49 mL of triethylenetetramine in 100 mL of demineralized water, adding 1.596 grams of  $CuSO_4$  and demineralized water until a final volume of one liter was reached. 40 mL of DI water was added to 200 mg of sediment, after which 10 mL of the Cu[Trien] solution was added. The samples were sonicated for 15 minutes to suspend the clay material. After sonication, the sediments were shaken for 30 minutes at 120 RPM. The samples were

centrifuged at 2680 g after which the supernatant was decanted, and analysed with ICP-OES. Additionally, Cu concentrations were measured by spectrophotometry at 577 nm (Ammann, 2005). The difference in Cu concentration before and after the reaction with the sediment samples was used to calculate the amount of adsorbed Cu and, by this, the CEC. All samples were analysed in triplicates.

#### 3.5. Analytical procedures

#### 3.5.1. C, N, S contents

For decalcification, 0.3 gram of the ground and freeze-dried sample was added into a 15 mL PP centrifuge tube and 7.5 mL of 1 M HCl was added. After the sample had stopped bubbling, tubes were closed and shaken for 12 hours. The supernatant was decanted after centrifugation at 2100 g for 5 minutes. Acid addition was repeated with a shorter reaction time of four hours. After removing the acid, the solid was washed with demineralized water in two cycles of resuspension and centrifugation. Finally, the C and N content was determined with an C/N analyzer in which the sample is combusted, the combustion gases are reduced over a Cu column, separated by gas chromatography and detected with a thermal conductivity detector.

Concentrations of C were determined before decalicification with a LECO SC632C/S analyser together with the S contents. The samples were combusted under an oxygen flow at  $\pm$  1350°C and C and S were measured as CO<sub>2</sub> and SO<sub>2</sub> with infrared detectors. The gas flows for purging and during measurement were adjusted to 2.5 $\pm$ 0.1 L/min.

#### 3.5.2. Aqueous solutions

The elemental composition of solutions was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Alkalinity was determined by titration with 0.1 M HCl and analysing the titration curve with the Gran method. A standard combined glass electrode with temperature sensor was used to determine pH.

For redox specific determination of Fe(II) and Fe(III) a modified ferrozine method was applied (Viollier et al., 2000). In brief, to 1.2 mL of the aqueous sample, 200  $\mu$ L of 0.01 M ferrozine reagent (monosodium salt hydrate of 3-(2-pyridyl)-5-6-bis (4-phenylsulfonic acid)- 1,2,4 triazine p-p'-disulfonice acid) was added plus 300  $\mu$ L demineralized water and 200  $\mu$ L 5 M ammonium acetate buffer with a pH of 9.5. The mixture was stirred and the absorbance was measured in polystyrene cuvettes at 562 nm with a photospectrometer. For determining total Fe, 300  $\mu$ L of 1.4 M hydroxylamine in 2 M HCl were added instead of demineralized water. In this case the buffer solution was added after 10 minutes reaction time and the formed Fe(II) was determined as described above.

#### 3.5.3. TXRF

Total reflection X-ray fluorescence (TXRF)was used to determine the Cu content of the sediment sample after the CEC determination. TXRF measurements were performed with a Bruker S2 Picofox. 500 mg of sample was dispersed in 10 mL of 1% Triton-X solution. To the suspension 100  $\mu$ L of 250 ppm Ga solution was added as internal standard. 5 $\mu$ L of the suspension was pipetted on a glass slide and analysed with TXRF.

# 4. Results and Discussion

#### **4.1.** *Pore water composition*

#### 4.1.1. Mechanical squeezing

The concentrations of the major cations and anions in the retrieved pore water from the samples in Zeeland are, in general, one or two orders of magnitude higher than in the Boom Clay in Mol or Essen (Tab. 4.1). Chloride concentrations are in the range between 70-96 % of seawater composition. This indicates that the seawater influence on the pore water composition in Boom Clay in Zeeland is significantly higher than in Mol or Essen.

When comparing to Cl concentrations, the pore water in the samples are relatively enriched in Ca and for samples 101 and 104 also in S. In contrast, sample 103 is relatively depleted in S with respect to seawater. Processes which can account for a decrease in dissolved S are precipitation of sulphates or microbial sulphate reduction when coupled to the precipitation of sulphides. The Mg/Cl ratios are similar or moderately higher in the different pore waters compared to seawater. In solutions from samples 101 and 104 this also holds for the Na/Cl and K/Cl ratios, while these ratios are lower than in seawater in sample 103. A shift in cation composition can be a result of cation exchange. For example, Ca might be exchanged against Na when initially the cation exchange complex is dominated by Ca and Na enters the sediment either by convective transport or by diffusion. This, in turn, can lead to an increase in Ca/Cl ratios and a decrease in Na/Cl and ratios and would provide an explanation for lower Na and K concentrations in sample 103 and higher Ca concentrations relative to seawater. This effect of cation exchange on cation composition in solution is expected at the forepart of a progressing salinity front. The base exchange index, BEX = Na + K + Mg - 1.0716 Cl in mEq (Stuyfzand, 2008), is negative for the solutions of all samples. A negative BEX indicates salinization of an aquifer when the deficit of marine cations is caused by cation exchange.

When using the Cl concentrations as an indicator for the seawater component in the pore water, the absolute enrichment in S and Ca in the pore water varies between 36 mM and 53 mM. In sample 104, the enrichment in S and Ca is very similar. This suggests that the pore water composition has been influenced by the oxidation of pyrite combined to the dissolution of CaCO<sub>3</sub> (Eq. 4.1).

**[4.1]** 4FeS<sub>2</sub> + 15O<sub>2</sub> + 10H<sub>2</sub>O + (16-8x) CaCO<sub>3</sub> → (16-8x) Ca<sup>2+</sup> + 4FeOOH + (16-16x) HCO<sub>3</sub><sup>-</sup> + 8x H<sub>2</sub>CO<sub>3</sub> + 8SO<sub>4</sub><sup>2-</sup>

Equation 4.1 presents the stoichiometry of the reaction when pyrite oxidation is coupled to the reduction of oxygen. The reaction of pyrite with oxygen generates H<sup>+</sup> which can be neutralized by the dissolution of calcium carbonates. The stoichiometric ratio between the produced  $Ca^{2+}$  and  $SO_4^{2-}$  varies between 1:1 and 2:1 depending on the final pH of the solution and the related carbonate speciation. The variable x in Eq. 4.1 is the fraction of produced H<sub>2</sub>CO<sub>3</sub>. At neutral pH, bicarbonate (HCO<sub>3</sub><sup>-</sup>) is the dominant dissolved carbonate species (x in Eq. 4.1 is approximately zero) resulting in a  $Ca^{2+}$  and  $SO_4^{2-}$  ratio of 2:1. When carbonic acid (H<sub>2</sub>CO<sub>3</sub>) is the dominant dissolved carbonate species (x in Eq. 4.1 is approximately zero) resulting in a  $Ca^{2+}$  and  $SO_4^{2-}$  ratio of 2:1. When carbonic acid (H<sub>2</sub>CO<sub>3</sub>) is the dominant dissolved carbonate species (x in Eq. 4.1 is approximately one), the stoichiometric ratio between produced  $Ca^{2+}$  and  $SO_4^{2-}$  ratio is one.

The concentrations of dissolved Ca and  $SO_4$  might be limited by the solubility of gypsum, implying that the extent of pyrite oxidation could be larger than inferred from the excess of Ca and  $SO_4$  with respect to seawater. If today's seawater is equilibrated with gypsum, the concentrations of Ca and  $SO_4$  will become about 33.0 mM and 50.5 mM, respectively (Holland, 1984). These values are exceeded by the measured concentrations in the collected pore water from samples 101 and 104. This implies that the solutions are supersaturated with respect to gypsum and precipitation of gypsum could have affected the pore water composition.

The pH in sample 103 and the alkalinity are lower than in seawater, indicating that part of the acid neutralization capacity associated with intruding seawater has been consumed. Acidification is more pronounced in the solutions obtained from samples 104 and 101 having an acidic pH value around

3.2-3.0. These values are significantly lower than the pH value of 6.5 in the solution from sample 103 and the pH values reported from Boom Clay pore water at other locations. Most likely, the low pH values of samples 104 and 101 do not reflect the acidity of the in-situ pore water but acidity has been produced in the solution after it had been squeezed out from the sample. A likely process producing acidity in the sample is the oxidation of dissolved Fe(II), S(-II) or particulate iron sulphides which are small enough to pass the pores of the clay and the porous steel plate. When the contact of the solution with atmospheric oxygen cannot be fully avoided, Fe(II) and S(-II) can react with oxygen which leads to the production of H<sup>+</sup>. We therefore suspect that the collected solution contained dissolved Fe(II), S(-II) or particulate Fe(II)-sulphides which became oxidized before analyses.

This interpretation is supported by the high Fe concentrations measured in the solution from sample 103. Assuming that all measured Fe is in the form of Fe(II) and that all alkalinity is related to carbonate species, the solution of sample 103 is close to equilibrium with siderite. Elevated Fe concentrations, in comparison to Boom Clay pore water in Essen or Mol, are also detected in the other two samples. In contrast, the solution from sample 103 has a near-neutral pH. During the squeezing of this sample, a thicker rubber stopper was used to close the bottle for a better protection of the solution indicates that the solutions from sample 104 and 101 could have been oxidized after collection because a thinner rubber stopper was applied. Furthermore, in none of the dilution experiments an acidic pH is detected providing additional support to the conclusion that the acidic pH in samples 104 and 101 does not reflect the in situ pore water acidity but is caused by oxidation of dissolved Fe(II) after collection.

Acid pore waters can be found in mine tailings and soils or aquifers which are affected by the oxidation of pyrite, often due to the excavation of pyrite-containing material and its exposure to the atmosphere. In these highly acidified environments, the acid neutralization capacity of the solids in the system is largely exhausted. Several geochemical reaction can contribute to the neutralization of acids in soils or sediments including: dissolution of carbonates or (hydr)oxides, protonation of functional groups at the solid surface, or the weathering of silicates. Based on the kinetics of the different neutralizing processes and their pH dependency, the different processes become relevant at different pH conditions. For acid mine tailings, the pH in the solution decreases along the series of minerals whose dissolution dominate acid neutralization: calcite> siderite> Al (hydr)oxide> Fe (hydr)oxide> silicates (Morin et al., 1988). The kinetics of the dissolution of carbonates or aluminium(hydr)oxides is usually fast enough to prevent a drop of pH values below values of 4.0. Lower pH values usually only occur when carbonates are depleted and solutions are characterized by high dissolved Fe and Al concentrations. The concentrations of Fe and Al are not elevated in the samples which also indicates that the acidity is produced after the solution has been removed from the clay matrix.

Table 4.1: Chemical composition of solution retrieved by mechanical squeezing from core sample 101 (slice 17 and 18), 104 (slice 9 and 11), and 103 (slices 11,12 and 13). The reported uncertainties indicate the variation between duplicate measurements. Evaluation of the calibration with independent standards were in the range of  $\pm$  5%. Measured concentrations are compared to those reported for Boom Clay pore water in Mol (De Craen et al., 2004) and in Essen (De Craen et al., 2006). For comparison, also the seawater composition according to Appelo and Postma (2005) is listed.

	Seawater	Sample 104	Sample 101	Sample 103	BC in Mol (B)	BC in Essen (B)
Na [mM]	485	443** ± 3	237** ± 4	133.1 ± 0.1	15.6	56
Cl [mM]	566	546** ± 2	408** ± 5	394.0 ± 0.1	0.5	44.1
S [mM]	29	65** ± 2	57** ± 1	3.9 ± 0.1	0.02*	4.2*
K [mM]	11	15.95** ± 0.02	10.4 ± 0.2	3.7 ± 0.2	0.2	0.7
Ca [mM]	11	47.0 ± 0.1	60.4 ± 0.7	69.7 ± 0.1	0.04 - 0.2	0.9
Mg [mM]	55	51.7 ± 0.3	42.3 ± 0.5	58.4 ± 0.1	0.05 - 0.2	2
Fe [µM]		297 ± 1	746 ± 12	3260 ± 0.1	6 - 50	70
рН	7.5 - 8.4	3.05	3.17	6.7	8.3-8.6	8.3-8.6
Alkal, [meq/ l]	2.47			0.55		

\*  $SO_4^{2^-}$  concentration. \*\* concentrations exceeded the calibration range and might have an error > 5%.

#### 4.1.2. Dilution method

The calculated composition of the pore waters, which has been deduced from the results of the dilution experiment, confirm the strong seawater signature in the Boom Clay pore water in Zeeland. The Cl concentrations vary between 73% and 103% of seawater concentration with the exception of sample 103A-01 (Tab. 4.2). This sample has been collected from the top of core 103A and was possibly experienced desiccation and oxidation. The latter is indicated by the presence of brown coloured material along fractures (see section 2.2). The solutions from sample 103A-01 differ also significantly from others with respect to other parameters, particularly the pH is with values above 10 considerably higher. The high pH value and the deviating composition of the solution from sample 103A-01 can be explained by evaporation and oxidation of the core top during storage. High pH values are a result of evaporation when part of the pore volume becomes unsaturated and  $CO_2$  escapes from the concentrating solution. When evaporation proceeds, precipitates can form which do not readily dissolve when water is added and which might trap Ca, Mg, or S. These precipitates include gypsum, silicates or, when also pyrite oxidation occurs, Fe oxides. Due to the complexity of these reactions, the solution of sample 103A-01 is not further considered when reconstructing the in-situ pore water.

The concentrations of cations in the solutions from the dilution experiments differ among each other and from those in the pore water obtained by the mechanical squeezing. Despite the variation a few trends become apparent: the relative concentrations of K are higher while Mg concentrations are lower in the dilution experiments than in the solutions obtained by mechanical squeezing. This trend is more pronounced when the dilution experiments are performed with NaHCO<sub>3</sub> than with demineralized water. Cation exchange might be the reason for the shift in cation concentrations during dilution. Addition of NaHCO<sub>3</sub> can displace the cation ratios in the solution which results in Na adsorption coupled to the desorption of other cations, such as  $K^+$ . Dilution of a solution, which is in equilibrium with an cation exchanger, can lead to a redistribution of cations. Depletion of Mg and release of K could therefore be ascribed to cation exchange reactions in the dilution experiments.

The S concentrations of the solutions from the dilution experiments vary substantially between samples and for sample 103-19a when demineralized water instead of  $NaHCO_3$  was used in the dilution experiments. Furthermore, the S concentrations of the solutions from sample 101-14 are about two times higher than in the solution squeezed out of core 101. This indicates that the

influence of processes producing or consuming dissolved S is very heterogeneous. It is remarkably that the S concentrations in the dilutions of sample 103-22 are all below detection limit and, hence, the solution is depleted in S with respect to seawater. This suggests that selective removal of S from solution, for example by sulphate reduction, can occur within the Boom Clay or that the seawater at the Boom Clay boundary is or was depleted in sulphate. The question whether the different processes leading to production or consumption of dissolved S occur in-situ or were induced by the storage and treatment of the cores, will be further discussed in section 5.

		1	Dem	ineralized	water			
	101-14	103A-01	103A-19a	103A-19b	103A-22	101-14	103A-19a	103A-22
Na [mM]	*	*	*	*	*	389	368	330
Cl [mM]	500	213	410	464	424	584	429	465
S [mM]	94.6	61.8	12.5	ND	ND	106	72	ND
K [mM]	90.4	261	74.5	124	34	57.2	50.0	33.4
Ca [mM]	53.6	ND	45.8	53.6	45.2	26.9	28.5	38.8
Mg [mM]	36.5	2.50	31.2	35.8	31.5	19.5	21.4	22.4
pH**	7.6	10.5	7.6	7.3	7.7	7.4	7.4	8.2

Table 4.2: Chemical composition of the in situ pore water calculated from the concentrations in the solutions retrieved from the dilution experiments after about 3 h reaction time.

\* due to high Na concentrations in the added solution, the Na concentrations in the in-situ pore water could not be calculated. ND = not determined because  $r^2 < 0.95$ . <sup>\*\*</sup> The pH value is the average value of all different dilutions and replicates.

#### 4.1.3. Time evolution of solution composition in the dilution experiments

The goal of performing the dilution experiment over a period of one month was to evaluate the contribution of heterogeneous reactions with slower kinetics to changing the composition of the pore water. This includes in particular dissolution and precipitation of reactive minerals and microbial processes. A general trend in the dilution experiment with demineralised water and sample KB101-14 is that the concentrations of cations are higher in solutions which were taken after a contact time of several days (Fig. 4.1). The concentrations of K and Na are higher after 3 days than after 3 hours but do not show a clear trend afterwards. In contrast, concentrations of Ca and Mg tend to increase over the whole period. The increase in Ca and Mg might be attributed to the dissolution of Ca/Mg-carbonates possibly coupled to cation exchange reactions. That is, a part of the Ca<sup>2+</sup> released upon dissolution of calcite might become exchanged against Mg<sup>2+</sup> at the cation exchange complex. The general increase in cation concentrations might also be caused by a delayed suspension of the material in demineralised water. Within 3 hours reaction time, equilibrium with the cation exchange complex might not be achieved because clay particles might not be completely dispersed. When the dispersion of clay aggregates continues over the next three days, additional cations might become released into solution.

Presence of bicarbonate in the solution can suppress the dissolution of carbonates and therefore explains why Ca and Mg concentrations do not increase over time when the dilution experiments are performed with bicarbonate solution. In these experiments, Ca and Mg concentrations tend to decrease over time. The decrease of Ca and Mg could be ascribed to the precipitation of sulphates and, by this, follow the trend in S concentrations in these samples. However, the Ca and S concentrations in the dilutions are so low that precipitation of gypsum can be excluded as the ion activity product does not exceed the solubility product of gypsum.

The difference between dilution experiments with bicarbonate solution and with demineralised water, in view of cation concentrations, is not always consistently reflected in the other samples KB103A-19a and KB103-22 (Figs. 4.2 and 4.3). That is, concentrations of Ca and Mg do not increase in all experiments with demineralised water and, hence, calcite dissolution does not affect the solution composition in all experiments. Differences in the extent of calcite dissolution in dilution experiments with these samples and those with sample KB101-14 could be explained by inhibition of

calcite dissolution by, for example, adsorption of phosphate (Berner, 1974). Most likely, however, the different extent of calcite dissolution is due to differences in calcite content. In other words, absence of calcite or lower calcite concentrations in samples KB103A-19a and KB103-22 can be a reason for lower rates or absence of Ca and Mg release during the dilution experiment with demineralised water.

In detail, in the experiments with sample KB103-22, the increase in Ca and Mg is very pronounced when demineralised water is added at the highest solid/solution ratio. In all other experiments, the increase in Ca and Mg is only moderate and whether demineralised water or bicarbonate solution is used in the experiments has no significant effect. In some individual experiments with sample KB103A-19a, the Ca and Mg concentrations increase by a factor of 2 or higher after 10 or 30 days reaction time. This increase is only observed when bicarbonate solution is added, while, in general, the increase in Ca and Mg concentrations is higher with demineralised water. This pronounced increase in Ca and Mg takes place in experiments with the lowest solid/solution ratio and also occurs in experiments with sample KB103A-19b with the lowest solid/solution ratio. In these experiments, the absolute Ca and Mg concentrations are lower than in the experiments with higher solid/solution ratios. Preliminary equilibrium calculations indicate that the solutions from experiments with bicarbonate solution with the lowest solid/solution ratios are undersaturated with respect to calcite even after 30 days reaction time. Hence, dissolution of calcite could possibly provide an explanation for the increase in Ca and Mg concentrations but it remains enigmatic why this increase occurs so abruptly and why Ca and Mg concentrations do not increase in experiments with demineralised water in which the degree of undersaturation with respect to calcite is higher.

In both samples, KB103A-19a and KB103-22, there is, in contrast to sample KB101-14, no significant difference in the increase of K with and without bicarbonate addition. The time evolution of concentrations in experiments with sample KB103-01 is complex, incongruent, and the changes are inhomogeneous. Throughout the experiments, the pH values remains at levels between 9.5 and 11.5 for the lowest and highest solid/solution ratio, respectively. The discussion of the underlying processes leading to the changes in solution composition for this sample falls out of the scope of this report as the alteration of the sample during storage is so severe that the processes during the dilution experiments have only very limited relevance for in-situ conditions.

Sulphate most likely accounts for the majority of dissolved S in the samples and its concentration shows in most cases higher dynamics compared to the time evolution of cation concentrations. This is an enigmatic observation as removal or release of sulphate has to be coupled to an increase or decrease of the concentrations of other ions in order to maintain charge balance. In sample KB103-19a and KB101-14, the common trend is that S concentrations increase in experiments with demineralised water during the first 10 days of reaction time. Afterwards, the concentrations tend to decrease. In experiments with bicarbonate, the S concentrations decrease and often reach values below detection limit. The difference in the dynamics of dissolved S between experiments with and without bicarbonate is enigmatic. Dissolution of sulphates, oxidation of sulphides, or desorption of sulphate can account for an increase in dissolved S concentrations. However, the levels of S concentrations are so high that any of the processes should be reflected in the concentrations of other major ions. For example, pyrite oxidation as a source for an increase in sulphate concentrations should either effect pH or the ion composition when the produced protons are neutralized by dissolution of carbonates. In view of the removal of dissolved sulphate, precipitation of sulphates should become reflected in the concentrations of the analysed cations. Precipitation of gypsum can be excluded anyway as the solutions are too diluted. Additionally, it is difficult to explain why removal of sulphate would be more efficient in experiments with demineralised water than with bicarbonate solution.

Biological activity might provide an explanation for the decrease in sulphate concentrations. A medium containing bicarbonate might be more favourable for microorganisms. Sulphate reducing bacteria have been identified in Boom Clay (Aerts et al., 2008) and they might become activated upon suspension. Also organic matter might become available for sulphate reducers upon suspension and hydrogen gas, which enters the experiments during manipulations in the glove box, can serve as an electron donor. However, only traces (<0.12 mM) of dissolved sulphide were detected at the end of the experiments, representing less than 1% of the initially dissolved S. The sulphide, produced by sulphate reduction, could react with iron phases forming iron sulphides. Unfortunately, our data do

not provide information about the change in the composition of solids. Hence, further investigation is required to unravel the processes controlling the S dynamics in these experiments.



Figure 4.1: Time evolution of the solution composition in the dilution experiments with sample KB 101-14. Concentrations are normalized to the values determined in the first sampling moment after 3h reaction time.



Figure 4.2: Time evolution of the solution composition in the dilution experiments with sample KB 103A-22. Concentrations are normalized to the values determined in the first sampling moment after 3h reaction time.



Figure 4.3: Time evolution of the solution composition in the dilution experiments with sample KB 103A-19a. Concentrations are normalized to the values determined in the first sampling moment after 3h reaction time.



Figure 4.4: Time evolution of the solution composition in the dilution experiments with sample KB 103A-19b. Concentrations are normalized to the values determined in the first sampling moment after 3h reaction time.



Figure 4.5: Time evolution of the solution composition in the dilution experiments with sample KB 103A-01. Concentrations are normalized to the values determined in the first sampling moment after 3h reaction time.

#### **4.2.** Sequential Extractions

The difference between the sum of the sequentially extracted Fe and the Fe which is independently extracted by aqua regia is under 20 % with the exception of sample KB 101-26 (29.3 %) and South-NL 19 (26.4 %). Fe contents calculated from the sum of the individual extraction steps tend to be smaller than those of the independent aqua regia extractions (Fig. 4.6). A systematic underestimation can be explained by loss of solids during the solid-solution separation steps between the different extractions. The content of total extractable Fe varies between 2.35 and 4.95 wt% (Fig. 4.7). The average concentration of extractable iron is  $3.56 \pm 0.61$  wt% at which the material from South NL has, with  $3.86 \pm 0.55$  wt%, a higher Fe concentration than the material from Zeeland with  $3.40 \pm 0.60$  wt%. However, the difference is not significant.

In the sequential extraction, the largest Fe fraction is extracted with aqua regia accounting for 68 - 81% in the samples from Zeeland and 57 - 72% in the samples from South-NL. This fraction represents detrital Fe which is typically bound in silicates. Concentrations of adsorbed Fe, which is extracted with MgCl<sub>2</sub>, is negligibly small and Fe associated with organic matter, extracted with pyrophosphate, is only a minor fraction in all samples. The Fe fraction, which is extracted with 1 M HCl over 4 hours, varies between 0.11 and 0.39 wt% and does not show a significant difference between the different locations. This fraction might include carbonates, such as siderite, FeS, or amorphous iron hydroxides, but also Fe which is released by partial dissolution from less reactive Fe phases. These phases include crystalline iron oxides or silicates and their partial dissolution cannot be completely suppressed under acidic conditions. Determination of Fe(II) and Fe(III) in the HCl extracts with the ferrozine method reveals that practically all extracted Fe is in the form of Fe(III). This implies, that dissolution of FeS and Fe carbonates has only marginally contributed to the Fe release during HCl extraction, and, consequently, it indicates that these solids only account for a minor portion of reactive Fe in the samples.

The largest fraction of reactive Fe is extracted with concentrated HNO<sub>3</sub>, which is representing Fe in pyrite. In general, pyrite contents are higher in the South-NL samples than in samples from Zeeland. In particular, pyrite contents in the samples from the deeper part of Boom Clay in South-NL are more than two times higher than in all other samples. In contrast, the amounts of Fe extracted with DCB are higher in samples from Zeeland compared to those from South-NL. Extraction with DCB targets crystalline iron (hydr)oxides, implying that Boom Clay in Zeeland might contain Fe(III) (hydr)oxides. It cannot be excluded that a part of the initially buried iron (hydr)oxides have not been prone to sulfidization during early diagenesis. However, it is more likely that iron oxides have formed after burial upon the oxidation of pyrite. Oxidation of pyrite in the samples from South-NL. However, the difference between the pyrite content in the deeper samples from South-NL (15 and 19) and that in the samples from Zeeland cannot be explained by oxidation of pyrite alone.

The differences in pyrite content between the upper and lower part of the Boom Clay in South-NL and between the Boom Clay from Zeeland are in agreement with the results from the study by (Koenen and Griffioen, 2014). Higher pyrite contents in the deeper part of Boom Clay in South-NL than in the upper part and the core from Zeeland was indicated by the S contents and results from XRD analysis. However, the statistical analysis do not reveal a general geographical trend that Boom Clay in the south-east of the Netherlands is generally richer in pyrite than Boom Clay in the south-west. No crystalline Fe(III) oxy(hydr)oxides were detected by XRD analysis of the samples from Zeeland and South-NL. It could be possible that the signal from the Fe(III) oxy(hydr)oxides was too small to be detected by XRD due to the low concentrations and possibly due to low crystallinity or small particle size.

In addition to Fe, the concentration of other elements in the extracts has been determined. Noticeable, Ca concentrations in the HCl extracts from samples of South-NL are, on average, about 10 times higher than those from Zeeland samples. Most of the Ca in this extracts originates from the dissolution of calcium carbonates, implying that the calcium carbonate content in the Zeeland samples is significantly lower than those from South-NL. Other significant differences between the locations include: 1) K concentrations in  $MgCl_2$  extract from Zeeland are about four times larger than those from South-NL indicating the exchange complex of material from Zeeland contains relatively more K<sub>2</sub> 2) Concentrations of Al in HNO<sub>3</sub> extracts of samples from Zeeland are, on average

more than two times larger than in extracts of samples from South NL. This implies that the  $HNO_3$  extract also dissolves Fe from clay minerals, but based on typical Al/Fe ratios in clay Fe from clay dissolution only accounts for less of 10% of the extracted Fe. High Al concentration in the  $HNO_3$  extracts suggests that clay minerals in Boom Clay in Zeeland are more prone to proton promoted dissolution than those in the Boom Clay in South-NL or that the Zeeland samples have a higher content of clay minerals. The latter is supported by the total Al contents in the South-NL samples than in samples from the Boom Clay in Zeeland (Koenen and Griffioen, 2014). 3) Also Mg concentrations in  $HNO_3$  extracts are almost four times higher when collected from samples in Zeeland than from samples in South-NL. The Mg concentrations could be effected by the previous MgCl<sub>2</sub> extractions possibly inducing MgSO<sub>4</sub> precipitation and might not directly reflect the dissolution of initially present solids.

In addition to sequential extractions, some samples have been subjected to an alternative destruction using a mixture of  $HClO_4$ ,  $HNO_3$  and HF. This destruction has not been performed in replicates so that the reliability of the results is uncertain. In general, Fe concentrations obtained from this alternative destruction procedure are lower than those from the sequential extraction. This is against expectation, but further measurements would be required in order to resolve this discrepancy.



Figure 4.6: Comparison of Fe contents in samples obtained from independent aqua regia extraction and from the sum of individual extractions.



Figure 4.7: Amount of iron extracted during the sequential extraction.  $MgCl_2 = 1 \text{ M}$  Magnesium chloride pH 7, HCl = 1 M HCl, 0.1 M Sodium pyrophosphate pH 10.4, DCB = Sodium citrate/dithionite solution buffered to a pH of 7.5 with NaHCO<sub>3</sub>, Aqua regia tot = independent aqua regia extraction of all extractable Fe.

#### 4.3.C, N, S Contents

Before decalcification, total C concentrations are in the range between 0.4-1.7 wt% and decrease in most of the samples due to removal of carbonates to 0.2-1.4 wt% (Fig. 4.8 and 4.9). The decrease in C content is most pronounced for samples from South-NL, while the change in C content upon decalcification is only marginal in samples from Zeeland. For most samples, even a higher C contents are obtained after decalcification. This phenomenon can be explained by preferential loss of solids with low C content during the calcification procedure. Assuming that the change in C content is predominately due to the removal of calcium carbonate, Boom Clay at the location in South-NL contains 2.8-9.1 wt% CaCO<sub>3</sub> (based on stoichiometric conversion from C to CaCO<sub>3</sub> content). In contrast, the CaCO<sub>3</sub> content at the location Zeeland is smaller than 1.4 wt% and in most samples, the loss in C content upon decalcification indicates that no CaCO<sub>3</sub> is present at all. The difference in CaCO<sub>3</sub> content between the two locations is in line with the difference in Ca concentrations of 1 M HCl extracts (see section 4.2).

Lower CaCO<sub>3</sub> contents in Boom Clay from Zeeland in comparison to Boom Clay from the location South-NL is in line with the trend that Boom Clay in the southwest has higher CaCO<sub>3</sub> contents than Bloom Clay in the southeast (Koenen and Griffioen, 2014). Aragonite and calcite were both detected by XRD analysis of a sample from the Zeeland core (Koenen and Griffioen, 2014) so that the absence of calcium carbonates in the core material, which is deduced from C analysis, is not confirmed by XRD analysis. Low CaCO<sub>3</sub> values in the Boom Clay samples from the drillings in Zeeland, being below the lower limit of 1 wt% reported for Boom Clay (De Craen et al., 2004), are an indication for the alteration of the sediments by oxidation. As discussed previously, oxidation of pyrite generates acid which can be neutralized by carbonates leading to dissolution of calcite and aragonite.

The C content after decalcification, representing organic C, is in all samples from Zeeland below 0.7 wt%, which is also lower than the range (1-5 wt%) reported by (De Craen et al., 2004) for the organic C content of Boom Clay. Decrease in organic C could also be a consequence of organic matter oxidation. However, comparison with the organic C content in samples from the location in Zeeland does not suggest that, in contrast to CaCO<sub>3</sub>, Boom Clay in Zeeland is depleted in organic C.

The S concentrations follow the trend in pyrite concentrations as inferred from the sequential extractions (Fig 4.8 and see section 4.2) with the exception of sample South-NL 15, in which the S contents are significantly smaller than expected from the pyrite content, which is derived from sequential Fe extraction. The average S content in the samples from South-NL tends with  $1.02 \pm 0.44$  wt% to be higher than in Boom Clay material from Zeeland ( $0.60 \pm 0.15$  wt%). Assuming that all S is bound in pyrite, these S contents correspond to pyrite concentrations of 1.9 and 1.1 wt%, respectively. These values are in good agreement to those obtained from sequential extractions: yielding pyrite concentrations of  $2.0 \pm 0.9$  wt% and  $0.9 \pm 0.3$  wt% for samples from Zeeland and South-NL, respectively. Also the increase in pyrite concentrations with depth in the Boom Clay in South-NL is similarly indicated by the S concentration profiles and the sequential extractions.

The N-content in the samples can be attributed to the nitrogen content of organic matter as the contribution of inorganic N, mostly in the form of adsorbed ammonium, to the total N content is only relevant in sediments with very low organic matter content (Müller, 1977). The  $C_{org}/N$  ratio is in the range of values reported for marine sediments (Müller, 1977; Ruttenberg and Goni, 1997). The average value of the  $C_{org}/N$  ratios in samples from South-NL, 14.3 ± 4.7, is larger compared to the value for samples from Zeeland,  $8.9 \pm 2.4$ . A  $C_{org}/N$  ratio of 6.6 is traditionally assigned to living marine phytoplankton (Redfield, 1934; Flemming 1940). After dying off, the decomposition of the organic matter ranges around 10 (Rullkötter, 2006), matching the  $C_{org}/N$  ratios measured in the Zeeland samples. Larger  $C_{org}/N$  ratios, as obtained for the Boom Clay samples from South-NL, might be a consequence of more pronounced diagenetic alterations or could indicate the input of a larger fraction of terrestrial organic matter with higher  $C_{org}/N$  ratios (Lamb et al., 2006).



Figure 4.8: Comparison of C contents in samples before and after decalcification (left panel) and  $FeS_2$  contents estimated from S contents or based on the results from sequential Fe extraction (right panel).



Figure 4.9: C, N, S contents of Boom Clay samples from Zeeland and South-NI.

#### **4.4.***Cation Exchange Capacity*

The Cu concentration of the solids after reaction with Cu solution correlates with the decrease in Cu solution but, on average, only about 75 %, were recovered in the solid phase (Fig. 4.10). This discrepancy could be due to an underestimation of the Cu content of solids by TXRF. Part of the emitted X-ray fluorescence by the adsorbed Cu might become absorbed upon the passage through overlying solids. In order to compensate for the effect, a correction factor needs to be determined with a set of calibration standards. However, a correction factor has not been independently determined for the used instrument so far. The Cu concentrations in the solutions have also been photometrically determined based on the blue colour of Cu complex in solution. For some solutions, the obtained Cu concentrations are comparable to those from ICP-OES measurement. However, in other cases large differences are obtained and the concentrations from replicate analyses vary considerably. It could be possible that the optical properties of the Cu complex in solution is altered depending on solution composition, in particular depending on salinity and pH, so that the concentrations obtained by ICP-OES are considered to be more reliable and are used here.

When the increase in concentration of cations in the Cu containing solutions is used to determine the CEC, systematically higher values are obtained. This discrepancy is most pronounced in the samples from South-NL and can be attributed to the release of cations from other sources than the exchange complex. In particular, dissolution of calcium carbonates can lead to an overestimation of the CEC. The content of calcium carbonates is higher in the Boom Clay in South-NL, which can explain the larger difference between the CEC values determined by Cu adsorption and release of cations.

The average CEC of Boom Clay material from the drillings in Zeeland is larger ( $18.5 \pm 4.5 \text{ meq} / 100\text{g}$ ) compared to the average CEC of Boom Clay samples from South-NL ( $11.5 \pm 1.3 \text{ meq} / 100\text{g}$ ), when using the values based on the decrease in Cu solution determined by ICP-OES. In general, these values are in the range, 7-30 meq / 100g, reported for the CEC of Boom Clay collected at different locations in Belgium (Honty, 2010).



Figure 4.10: Cation exchange capacity of Boom Clay samples from Zeeland and South NL. The CEC was determined based on the change of Cu concentration in the solution (measured by ICP-OES), the Cu content of the samples after treatment with Cu solution, and the release of cations upon reaction with Cu solution. Error bars are standard deviations of triplicate analyses.

# 5. Conclusions

The composition of solutions retrieved by mechanical squeezing and the composition of in-situ pore water, which is deduced from dilution experiments, show a considerable variability. Nevertheless, some main trends can be identified and can be related to processes in Boom Clay controlling the pore water composition.

In comparison to Boom Clay pore water in Essen or Mol, the salinity in the pore water at the location in Zeeland is significantly higher and approaches seawater level in some samples. Boom Clay has been deposited in a marine environment but the high salinity is most likely not a fossil signal. In Mol and Essen, most of the dissolved salts have left the Boom Clay and today's pore water has a fresh water signature. In a previous TNO report (Rijkers et al., 1998), elevated salinity was reported in the upper 10-12 m of Boom Clay in a core which was retrieved about 9 km south-west of the drillings presented in this study. The depth profile of the salinity was interpreted as a recent process of a progressing salinity front. The core sections investigated in this study were collected from different depth intervals but nevertheless do not show a clear trend with respect to salinity. However, the thickness of Boom Clay in these drillings is less than 14 m which is in the range of the reported progress of the salinity front in the TNO report. Hence, diffusive intrusion of seawater ions might affect the Boom Clay pore composition in all core section from the location in Zeeland which are investigated in this study.

In a first instance, dissolved inorganic constituents would be expected to advance with a comparable pace within a porous medium, provided that the constituents behave conservatively and do not interact with the solid phase. Assuming that the ion composition at the Boom Clay boundary in Zeeland resembles or resembled seawater, relative enrichment or depletion of ions with respect to chloride are consequently reflecting heterogeneous reactions between solids and dissolved constituents. In the forefront of a progressing salinity plume, cation exchange might cause a release of adsorbed Ca on the expense of Na, K, or Mg and might account for the relative enrichment in Ca and depletion of Na, K, and Mg in the solution obtained from samples of drilling 103 by mechanical squeezing. The investigated core section is about 9 m below the boundary between Boom Clay and the Breda formation, which is the largest distance of all core sections investigated here. The distance of 9 m corresponds to the progression of the salinity front as reported in the previous TNO report and hence, the cation composition in the solution from collected from core 103 could be a result of cation exchange at the forefront of a progressing salinity plume. In general, all pore waters obtained by mechanical squeezing have a negative base exchange index, which is an indicator for salinization in aquifers (Stuyfzand, 2008). The potential effect of exchange reactions on cation composition in solutions is also illustrated by the results from the dilution experiments: dilution with demineralized water can bias solution composition towards monovalent cations, while dilution with NaHCO<sub>3</sub> solution can lead to an increase of cations in the solution due to exchange against Na.

Very important processes in view of pore water composition and reactive mineral assemblage are redox reactions involving Fe and S. Most of the analysed solutions indicate a relative enrichment of the solution in sulphate, which is an indicator for pyrite oxidation (De Craen et al., 2004). However, some solutions indicate that the Boom Clay pore water is relatively depleted with respect to sulphate. Removal of sulphate from solution is most likely a consequence of microbial sulphate reduction coupled to sulphide precipitation. Although indications for the oxidation and reduction of S are given, the location and timing of these redox reactions cannot be unequivocally constrained based on our results. The time evolution of sulphate concentrations in the dilution experiments demonstrates the potential for sulphate removal in Boom Clay. However, the relevance of this process in the undisturbed Boom Clay is questionable. Sulphate reduction might have been stimulated in the dilution experiments by the supply of H<sub>2</sub> during the preparation of the experiments in the glove box and by the dispersion of the material. Dispersion eliminates the space and transport limitations of microbial growth in Boom Clay and might increase the bioavailability of organic matter. It could be possible that the water at the Boom Clay boundaries is or has been already depleted in sulphate due to sulphate reduction during the subsurface migration of the solution.

A similar ambiguity remains regarding the location and timing of pyrite oxidation. Most likely, two of the three solutions obtained by mechanical squeezing have been affected by oxidation of Fe(II) or FeS by atmospheric oxygen. Oxidation of the solution after collection can account for the low pH of

the solutions but cannot explain the enrichment in sulphate alone. Solutions enriched with sulphate also exhibit high Ca concentrations which indicate that the acidity produced by pyrite oxidation has been neutralized by calcite dissolution. The enrichment of sulphate and Ca in the solutions reaches values that precipitation of gypsum, as another accompanying process of pyrite oxidation affecting pore water composition, cannot be excluded. However, it remains unresolved whether the oxidation of pyrite has occurred in the cores during storage or whether oxidation of Boom Clay happens of has happened in-situ. Progress of an oxidation front into Boom Clay has been investigated in the HADES laboratory (De Craen et al., 2011). Decades of oxygen exposure altered the mineral composition only very close to the interface, while oxidation of pyrite was reflected in the pore water composition over a distance of 1 m. However, it is unclear whether the changes in solution composition were caused by diffusion of the reaction products (Ca and sulphate) or were produced in situ due to the invasion of oxygen.

Intrusion of dissolved oxygen into Boom Clay is controlled by the kinetics of oxygen consuming reactions in relation to its diffusive transport. It is unclear to which extent pyrite and possibly organic matter have to be depleted before relevant amounts of oxygen can pass and can proceed beyond the zone of obvious mineral alteration. The presence of a distinct vertical oxidation front in terms of a colour change from grey to brown has not been observed during the slicing of the cores. Nevertheless, oxidized patches were recognized also in the interior of the cores. Additionally, iron oxide production was noticed at the surface of cores which is most likely the result of oxidation during core storage. This observation together with the large variability in S and Ca contents in solutions over relative short vertical and horizontal distances (KB103\_19a and KB103\_19b) suggests that relative enrichment in sulphate and Ca in the pore waters is a consequence of oxidation during core storage and presumably not an indicator of in-situ oxidation. This suggestion does not exclude the possibility that the Boom Clay in Zeeland has been subjected to intrusion of oxidants in the past, possibly when part of the Boom Clay has been eroded.

The assemblage of reactive minerals points towards oxidation of pyrite in the Boom Clay in Zeeland. The initial composition of the Boom Clay after deposition is not known. However, comparison of the solid phase composition at the location in Zeeland with that in South-NL or locations in Belgium suggest that the Boom Clay in Zeeland is depleted in calcium carbonates, pyrite and organic matter and is enriched in iron oxides. All these trends can be attributed to the oxidation of pyrite, and it cannot be excluded that these modifications have been caused by oxidation during core storage. However, the solid phase composition is less sensitive to oxidation artefacts than the pore water composition and it is unlikely that the above mentioned changes have been established during storage. It could be possible that the solid phase alterations upon oxidation are not an indicator of ongoing oxidation but they might be a fossil signal. Oxidation of Boom Clay could have taken place in Zeeland during the erosion of the upper part of the Boom Clay. However, further research is required to obtain a better understanding whether or not oxidation events in the Boom Clay have occurred and in which time periods this has happened..

Increase of salinity and alterations of solid phase and pore water upon pyrite oxidation and accompanying mineral transformations can have consequences of the mobility of radionuclides in Boom Clay. The speciation of dissolved radionuclides in fresh water and saline water can be different due to the formation of aqueous complexes of the radionuclides with highly abundant ions such as chloride, which in turn could interfere with radionuclide adsorption. Retardation of radionuclides due to adsorption could also be impeded due the competition of other dissolved ions. Depletion of calcium carbonates has consequences for the pH buffering in the system. When all calcium carbonates are removed, acidity production can induce a decrease in pH until other acid neutralizing processes, such as silicate weathering, become relevant. A loss in pyrite and organic matter reduces the electron accepting capacity of Boom Clay, implying that the redox conditions in the system might respond faster on the intrusion of oxidants. Finally, many metal ions and metalloids have a high affinity for iron (hydr)oxides and freshly precipitated iron (hydr)oxides can substantially retard the migration of radionuclides when present in Boom Clay.

Open questions which have been raised by this study:

Is the intrusion of a salinity front into Boom Clay a local phenomenon or a widely spread feature of Boom Clay in the Netherlands?

Is it possible that relevant amounts of oxygen can intrude Boom Clay and lead to the alteration of pore water composition beyond the oxidation front which is indicated by quantitative transformation of Fe(II) to Fe(III) minerals?

Did oxidation events in the past cause depletion of pyrite, calcite, and organic matter in the Boom Clay in Zeeland and have comparable events changed the reactive mineral composition at other locations in the Netherlands?

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# 7. Appendix

Table A 1.1: Results sequential Fe extraction. The method related to each extraction step is described in Tab. 2.5. Fe total = Fe content obtained from independent extraction with aqua regia. Stddev = standard deviation of triplicate analyses.

Sample Name	Fe step 1 % wt	Stddev	Fe step 2 % wt	Stddev	Fe step 3 % wt	Stddev	Fe step 4 % wt	Stddev	Fe step 5 % wt	Stddev	Fe step 6 % wt	Stddev	Fe total % wt
КВ 101-14	0.004	0.0001	0.211	0.018	0.030	0.007	0.100	0.004	0.601	0.066	2.901	0.051	
KB 101-26	0.005	0.0004	0.127	0.015	0.011	0.003	0.069	0.008	0.403	0.089	1.735	0.178	3.157
KB 103A-1	0.004	0.0001	0.376	0.029	0.074	0.043	0.263	0.005	0.422	0.027	2.608	0.034	4.305
KB 103A-19a	0.004	0.0001	0.294	0.028	0.040	0.002	0.122	0.012	0.573	0.054	2.217	0.077	3.752
KB 103A-19b	0.004	0.0000	0.314	0.005	0.042	0.005	0.143	0.039	0.246	0.030	3.225	0.121	4.083
KB 103A-22	0.006	0.0028	0.317	0.035	0.026	0.004	0.204	0.098	0.278	0.144	2.463	0.157	3.906
КВ 104-10	0.006	0.0014	0.138	0.021	0.013	0.001	0.078	0.016	0.301	0.054	2.247	0.061	3.276
KB 104-24	0.005	0.0001	0.109	0.020	0.012	0.003	0.092	0.010	0.342	0.031	1.873	0.012	2.887
South-NL 2	0.004	0.0002	0.320	0.035	0.040	0.018	0.039	0.013	0.512	0.083	2.370	0.114	4.015
South-NL 9	0.004	0.0004	0.372	0.015	0.038	0.005	0.047	0.003	0.618	0.038	2.303	0.024	3.360
South-NL 15	0.004	0.0001	0.386	0.013	0.045	0.022	0.046	0.002	1.322	0.334	2.383	0.044	3.929
South-NL 19	0.004	0.0005	0.287	0.053	0.047	0.025	0.040	0.004	1.217	0.010	2.196	0.221	4.947

### Table A 1.2: Results C,S and C,N analyses.

Sample Name	C without decalcification % wt	S without decalcification % wt	C after decalcification % wt	N after decalcification % wt
KB 101-14	0,48	0,87	0,41	0,042
KB 101-26	0,41	0,48	0,24	0,031
KB 103A-01	0,66	0,54	0,69	0,067
KB 103A-19a	0,39	0,78	0,21	0,038
KB 103A-19b	0,54	0,57	0,57	0,057
KB 103A-22	0,62	0,50	0,65	0,069
KB 104-10	0,37	0,47	0,44	0,048
KB 104-24	0,41	0,61	0,43	0,046
South-NL 02	1,35	0,60	0,32	0,026
South-NL 09	1,39	0,82	0,61	0,042
South-NL 15	1,66	1,03	0,57	0,042
South-NL 19	1,73	1,63	1,40	0,081

#### Table A 1.3: Results CEC determination.

Sample Name	CEC [meq/100 g]	STDV	CEC [meq/100 g]	STDV	CEC [meq/100 g]	STDV
		5100		5100		5100
KB 101-14	10,2	2,1	20,0	0,8	27,9	0,8
KB 101-26	9,1	1,2	13,2	0,3	19,3	0,8
KB 103A-01	18,2	1,8	23,0	2,5	34,6	2,2
KB 103A-19a	7,9	0,9	11,2	0,5	14,6	0,5
KB 103A-19b	17,1	3,7	23,8	0,4	29,0	1,2
KB 103A-22	14,3	1,6	17,2	1,7	25,4	2,6
КВ 104-10	14,5	1,0	18,6	1,2	25,6	1,9
КВ 104-24	16,0	3,1	21,2	1,3	27,4	0,1
South-NL 02	5,0	0,9	10,4	1,5	20,9	0,6
South-NL 09	8,1	1,7	10,6	2,8	22,9	1,2
South-NL 15	8,3	0,8	13,3	0,2	23,2	1,4
South-NL 19	6,7	2,9	11,7	1,2	20,5	0,9

dilution	Time	Sample Name	Solution	S/L g/L	B mg/L	Ba mg/L	Ca mg/L	Cl mg/L	Fe mg/L	K mg/L	Li mg/L	Mg mg/L	Mn mg/L	Mo mg/L	Na mg/L	S mg/L	Si mg/L	Sr mg/L	Zn mg/L
1	то	KB 101-14	NaHCO3	25	0.030	0.290	1.060	9.000	0.080	1.650	0.010	0.450	b.d.	b.d.	28.470	1.630	0.040	0.010	0.010
1	то	KB 101-14	NaHCO3	25	0.020	0.170	1.010	8.140	0.080	1.590	0.010	0.430	b.d.	b.d.	28.210	1.530	0.040	0.010	0.010
1	то	KB 101-14	NaHCO3	50	0.020	0.070	1.690	14.320	0.080	2.830	0.010	0.760	b.d.	b.d.	30.080	2.960	0.050	0.020	0.010
1	то	KB 101-14	NaHCO3	50	0.020	0.090	1.860	14.570	0.070	2.740	0.010	0.810	b.d.	b.d.	31.150	3.250	0.060	0.020	0.010
1	то	KB 101-14	NaHCO3	200	0.030	0.070	5.730	48.130	0.080	7.330	0.010	2.830	b.d.	b.d.	47.620	13.490	0.140	0.080	0.020
1	то	KB 101-14	NaHCO3	200	0.030	0.070	5.850	49.160	0.080	7.380	0.010	2.860	b.d.	b.d.	48.160	13.650	0.130	0.080	0.020
1	то	KB 103 A 01	NaHCO3	25	0.020	0.080	0.390	3.690	0.090	1.160	0.010	0.020	b.d.	b.d.	29.290	0.920	0.450	0.000	0.010
1	то	KB 103 A 01	NaHCO3	25	0.020	0.050	0.430	3.470	0.090	1.200	b.d.	0.020	b.d.	b.d.	29.190	0.870	0.450	0.000	0.020
1	то	KB 103 A 01	NaHCO3	50	0.030	0.100	0.300	5.270	0.100	1.340	0.010	0.030	b.d.	b.d.	31.620	1.260	0.600	0.000	0.010
1	то	KB 103 A 01	NaHCO3	50	0.030	0.110	0.260	5.700	0.100	1.270	0.010	0.030	b.d.	b.d.	31.210	1.300	0.630	0.000	0.010
1	то	KB 103 A 01	NaHCO3	200	0.090	0.060	0.150	15.900	0.170	1.340	0.010	0.040	b.d.	b.d.	38.280	3.810	1.130	0.000	0.030
1	то	KB 103 A 01	NaHCO3	200	0.160	0.050	0.150	24.750	0.170	1.630	0.010	0.050	b.d.	b.d.	46.760	4.280	1.180	0.000	0.020
1	то	KB 103A 19b	NaHCO3	25	0.010	0.080	0.830	6.540	0.080	0.990	0.010	0.350	b.d.	b.d.	22.020	0.156	0.040	0.010	0.010
1	то	KB 103A 19b	NaHCO3	25	0.010	0.080	0.940	7.550	0.080	1.360	0.010	0.400	b.d.	b.d.	22.890	0.148	0.040	0.010	0.020
1	то	KB 103A 19b	NaHCO3	50	0.010	0.100	1.560	12.800	0.080	1.980	0.010	0.680	b.d.	b.d.	24.830	0.240	0.050	0.020	0.010
1	Т0	KB 103A 19b	NaHCO3	50	0.010	0.100	1.530	11.790	0.080	2.120	0.010	0.690	b.d.	b.d.	23.840	0.250	0.070	0.020	0.010
1	Т0	KB 103A 19b	NaHCO3	200	0.020	0.050	4.660	37.650	0.190	3.220	0.010	2.250	b.d.	b.d.	32.640	0.440	0.100	0.060	0.020
1	Т0	KB 103A 19b	NaHCO3	200	0.020	0.060	4.950	40.990	0.130	3.560	0.010	2.370	b.d.	b.d.	33.700	0.460	0.110	0.070	0.020
1	Т0	KB 103A 19a	NaHCO3	25	0.030	0.180	0.930	7.930	0.080	1.350	0.010	0.390	b.d.	b.d.	23.970	0.290	0.040	0.010	0.010
1	Т0	KB 103A 19a	NaHCO3	25	0.020	0.090	0.990	7.060	0.080	1.530	0.010	0.420	b.d.	b.d.	23.700	0.300	0.050	0.010	0.010
1	Т0	KB 103A 19a	NaHCO3	50	0.010	0.060	1.450	11.050	0.080	1.490	0.010	0.620	b.d.	b.d.	24.010	0.185	0.030	0.020	0.010
1	Т0	KB 103A 19a	NaHCO3	50	0.010	0.150	1.440	11.320	0.080	1.600	0.010	0.640	b.d.	b.d.	23.810	0.178	0.040	0.020	0.010
1	то	KB 103A 19a	NaHCO3	200	0.020	0.080	4.260	35.340	0.300	3.060	0.010	2.090	b.d.	b.d.	31.810	0.390	0.070	0.060	0.020
1	Т0	KB 103A 19a	NaHCO3	200	0.020	0.120	3.970	32.750	0.250	2.940	0.010	1.910	b.d.	b.d.	30.800	0.360	0.060	0.050	0.010

Table A 1.4: Composition solution from dilution experiments. Timesteps correspond to about 3h, 3d, 10d, and 30d. Concentrations with a dilution value of 1 have to multiplied by a factor of 10 to obtain the concentrations in the solution; b.d. = below detection limit.

dilution	Time	Sample Name	Solution	S/L g/L	B mg/L	Ba mg/L	Ca mg/L	Cl mg/L	Fe mg/L	K mg/L	Li mg/L	Mg mg/L	Mn mg/L	Mo mg/L	Na mg/L	S mg/L	Si mg/L	Sr mg/L	Zn mg/L
10	то	KB 101-14	demi	25	0.090	0.480	5.130	104.630	1.230	10.470	0.080	2.350	b.d.	b.d.	44.180	18.610	0.600	b.d.	0.120
10	то	KB 101-14	demi	25	0.030	0.110	6.130	86.310	1.220	10.220	0.080	2.720	b.d.	b.d.	41.230	15.060	0.540	0.010	0.110
10	то	KB 101-14	demi	50	0.110	0.850	11.090	139.290	1.210	17.870	0.080	5.430	b.d.	b.d.	71.600	24.680	0.610	0.090	0.120
10	то	KB 101-14	demi	50	0.050	0.100	11.180	131.710	1.230	17.710	0.080	5.570	b.d.	b.d.	71.210	23.690	0.610	0.080	0.150
10	Т0	KB 101-14	demi	200	0.220	1.020	47.670	462.120	1.690	49.700	0.120	25.750	b.d.	b.d.	234.600	110.290	1.010	0.600	0.160
10	то	KB 101-14	demi	200	0.210	0.630	43.980	436.580	1.980	47.820	0.110	24.010	b.d.	b.d.	228.720	104.360	1.010	0.560	0.210
10	то	KB 103A 19a	demi	25	0.100	0.800	5.820	80.660	1.210	8.490	0.080	2.760	b.d.	b.d.	41.980	10.940	0.530	0.020	0.120
10	Т0	KB 103A 19a	demi	25	0.020	0.080	6.000	68.940	1.230	10.390	0.080	2.720	b.d.	b.d.	39.610	13.380	0.560	0.010	0.140
10	то	KB 103A 19a	demi	50	0.140	0.780	12.610	139.480	1.240	17.450	0.080	6.200	b.d.	b.d.	74.460	27.910	0.620	0.110	0.240
10	то	KB 103A 19a	demi	50	0.120	0.850	10.840	134.880	1.230	18.260	0.070	5.290	b.d.	b.d.	72.810	22.400	0.600	0.090	0.130
10	Т0	KB 103A 19a	demi	200	0.220	0.550	48.350	435.070	1.510	48.380	0.120	25.670	b.d.	b.d.	219.370	101.850	0.910	0.610	0.230
10	то	KB 103A 19a	demi	200	0.220	0.630	47.420	442.010	1.570	49.590	0.110	25.050	b.d.	b.d.	233.570	102.650	1.000	0.600	0.210
10	Т0	KB 103 A - 22	demi	25	0.120	0.860	8.240	84.110	1.260	7.220	0.070	2.950	b.d.	b.d.	38.110	b.d.	0.630	0.040	0.190
10	то	KB 103 A - 22	demi	25	0.090	0.500	6.660	67.660	1.240	5.040	0.070	2.500	b.d.	b.d.	28.440	b.d.	0.550	0.020	0.200
10	то	KB 103 A - 22	demi	50	0.030	0.080	12.400	118.140	1.250	9.560	0.080	4.760	b.d.	b.d.	46.530	b.d.	0.660	0.080	0.160
10	то	KB 103 A - 22	demi	50	0.110	0.940	12.080	118.670	1.330	9.270	0.080	5.100	b.d.	b.d.	47.360	b.d.	0.630	0.090	0.150
10	то	KB 103 A - 22	demi	200	0.170	1.300	37.380	336.950	2.290	26.090	0.090	17.710	0.050	b.d.	124.560	b.d.	0.860	0.480	0.270
10	Т0	KB 103 A - 22	demi	200	0.150	0.990	39.440	341.940	1.310	27.310	0.090	17.630	0.030	b.d.	125.850	b.d.	0.770	0.480	0.240
10	Т0	KB 103 A - 22	NaHCO3	25	0.100	0.620	9.060	75.260	1.230	6.590	0.070	3.890	b.d.	b.d.	214.880	b.d.	0.590	0.050	0.250
10	Т0	KB 103 A - 22	NaHCO3	25	0.220	0.530	8.400	66.760	1.360	5.720	0.070	3.640	b.d.	b.d.	215.650	b.d.	0.610	0.040	0.270
10	то	KB 103 A - 22	NaHCO3	50	0.100	0.140	15.420	107.530	1.670	9.300	0.070	6.850	b.d.	b.d.	230.590	b.d.	0.690	0.140	0.390
10	то	KB 103 A - 22	NaHCO3	50	0.130	0.820	14.540	116.730	1.330	9.090	0.070	6.590	b.d.	b.d.	233.180	b.d.	0.700	0.140	0.440
10	Т0	KB 103 A - 22	NaHCO3	200	0.180	0.380	52.540	379.850	1.260	32.540	0.090	23.870	0.010	b.d.	304.960	2.200	1.030	0.660	0.350
10	то	KB 103 A - 22	NaHCO3	200	0.110	0.070	45.350	356.660	1.690	26.690	0.090	21.870	0.080	b.d.	302.600	b.d.	1.110	0.580	0.430

dilution	Time	Sample Name	Solution	S/L g/L	B mg/L	Ba mg/L	Ca mg/L	Cl mg/L	Fe mg/L	K mg/L	Li mg/L	Mg mg/L	Mn mg/L	Mo mg/L	Na mg/L	S mg/L	Si mg/L	Sr mg/L	Zn mg/L
1	T1	KB 101-14	NaHCO3	25	0.010	0.110	1.100	7.560	0.090	1.900	0.010	0.430	b.d.	b.d.	24.170	1.710	0.100	0.010	0.020
1	T1	KB 101-14	NaHCO3	25	0.010	0.060	1.040	6.690	0.080	1.610	0.010	0.420	b.d.	b.d.	23.640	1.630	0.090	0.010	0.020
1	T1	KB 101-14	NaHCO3	50	0.010	0.550	1.750	14.280	0.080	2.960	0.010	0.730	b.d.	b.d.	28.140	3.280	0.120	0.020	0.030
1	T1	KB 101-14	NaHCO3	50	0.020	0.120	2.050	12.930	0.080	2.970	0.010	0.810	b.d.	b.d.	27.040	3.820	0.120	0.020	0.020
1	T1	KB 101-14	NaHCO3	200	0.030	0.140	5.910	44.240	0.080	7.400	0.010	2.750	b.d.	b.d.	43.560	14.880	0.210	0.080	0.030
1	T1	KB 101-14	NaHCO3	200	0.030	0.180	6.260	45.470	0.080	7.840	0.010	2.890	b.d.	b.d.	44.560	15.010	0.200	0.080	0.030
1	T1	KB 103 A 01	NaHCO3	25	0.040	0.080	0.330	5.280	0.140	1.540	0.010	0.060	b.d.	b.d.	25.690	0.960	0.790	0.000	0.180
1	T1	KB 103 A 01	NaHCO3	25	0.030	0.040	0.090	3.270	0.100	0.990	0.010	0.020	b.d.	b.d.	24.580	0.890	0.740	b.d.	0.020
1	T1	KB 103 A 01	NaHCO3	50	0.070	0.080	0.080	8.950	0.120	1.070	0.010	0.020	b.d.	b.d.	27.720	1.480	1.120	b.d.	0.020
1	T1	KB 103 A 01	NaHCO3	50	0.090	0.030	0.070	10.800	0.130	1.130	0.010	0.030	b.d.	b.d.	28.910	1.660	1.250	b.d.	0.020
1	T1	KB 103 A 01	NaHCO3	200	0.160	0.110	2.550	9.860	25.230	11.520	0.040	6.980	0.040	b.d.	43.330	6.250		0.090	0.080
1	T1	KB 103 A 01	NaHCO3	200	0.200	0.100	3.520	10.050	11.480	6.770	0.030	4.100	0.030	b.d.	45.100	6.390		0.110	0.080
1	T1	KB 103A 19b	NaHCO3	25	0.030	0.110	1.050	6.910	0.080	1.750	0.010	0.450	b.d.	b.d.	23.560	b.d.	0.180	0.010	0.020
1	T1	KB 103A 19b	NaHCO3	25	0.020	0.060	1.100	7.690	0.090	1.750	0.010	0.460	b.d.	b.d.	23.820	b.d.	0.130	0.010	0.030
1	T1	KB 103A 19b	NaHCO3	50	0.020	0.130	1.440	13.850	0.080	2.740	0.010	0.670	b.d.	b.d.	25.440	0.320	0.200	0.020	0.030
1	T1	KB 103A 19b	NaHCO3	50	0.020	0.130	1.490	12.750	0.080	2.820	0.010	0.700	b.d.	b.d.	24.870	0.350	0.190	0.020	0.020
1	T1	KB 103A 19b	NaHCO3	200	0.040	0.100	4.430	42.100	0.120	4.530	0.010	2.180	b.d.	b.d.	34.490	0.620	0.410	0.060	0.020
1	T1	KB 103A 19b	NaHCO3	200	0.030	0.100	4.570	44.480	0.100	4.490	0.010	2.300	b.d.	b.d.	34.950	0.640	0.370	0.060	0.020
1	T1	KB 103A 19a	NaHCO3	25	0.020	0.120	0.960	6.970	0.080	1.850	0.010	0.430	b.d.	b.d.	22.800	0.340	0.110	0.010	0.020
1	T1	KB 103A 19a	NaHCO3	25	0.010	0.230	0.980	7.910	0.080	2.570	0.010	0.440	b.d.	b.d.	22.800	0.360	0.110	0.010	0.020
1	T1	KB 103A 19a	NaHCO3	50	0.010	0.100	1.510	11.260	0.080	2.310	0.010	0.650	b.d.	b.d.	23.870	b.d.	0.220	0.020	0.020
1	T1	KB 103A 19a	NaHCO3	50	0.020	0.150	1.680	12.220	0.130	2.340	0.010	0.690	b.d.	b.d.	24.120	0.270	0.260	0.020	0.020
1	T1	KB 103A 19a	NaHCO3	200	0.040	0.070	4.440	42.540	0.250	4.200	0.010	2.240	0.000	b.d.	34.150	0.620	0.440	0.060	0.020
1	T1	KB 103A 19a	NaHCO3	200	0.040	0.280	4.640	44.390	0.280	4.300	0.010	2.300	0.000	b.d.	34.740	0.640	0.440	0.060	0.030

dilution	Time	Sample Name	Solution	S/L g/mL	B mg/L	Ba mg/L	Ca mg/L	CI mg/L	Fe mg/L	K mg/L	Li mg/L	Mg mg/L	Mn mg/L	Mo mg/L	Na mg/L	S mg/L	Si mg/L	Sr mg/L	Zn mg/L
10	T1	KB 101-14	demi	25	0.180	1.060	6.450	94.250	1.300	16.130	0.080	2.910	b.d.	b.d.	49.290	15.550	1.000	0.020	0.540
10	T1	KB 101-14	demi	25	0.200	0.900	7.330	91.670	1.310	15.790	0.080	3.200	b.d.	b.d.	53.740	18.500	0.930	0.030	0.530
10	T1	KB 101-14	demi	50	0.220	1.090	14.420	146.770	1.280	24.590	0.090	6.670	b.d.	b.d.	87.100	36.150	1.110	0.120	0.550
10	T1	KB 101-14	demi	50	0.260	1.270	14.190	145.310	1.290	24.050	0.080	6.610	b.d.	b.d.	89.810	38.440	1.270	0.130	0.530
10	T1	KB 101-14	demi	200	0.330	0.520	62.410	479.180	1.470	58.430	0.130	31.860	0.000	b.d.	270.360	183.150	2.520	0.760	0.570
10	T1	KB 101-14	demi	200	0.360	0.300	57.610	480.170	1.400	57.820	0.130	29.860	b.d.	b.d.	270.970	172.780	2.740	0.680	0.560
10	T1	KB 103A 19a	demi	25	0.180	1.460	8.120	85.470	1.320	13.760	0.080	3.540	b.d.	b.d.	52.840	20.780	1.130	0.050	0.550
10	T1	KB 103A 19a	demi	25	0.210	1.190	7.580	83.290	1.290	14.620	0.080	3.420	b.d.	b.d.	51.070	20.440	0.920	0.040	0.560
10	T1	KB 103A 19a	demi	50	0.200	0.750	16.190	140.080	1.290	23.720	0.090	7.370	b.d.	b.d.	86.840	44.960	1.470	0.140	0.560
10	T1	KB 103A 19a	demi	50	0.180	0.210	13.890	147.890	1.290	24.120	0.090	6.560	b.d.	b.d.	86.460	33.740	1.190	0.100	0.560
10	T1	KB 103A 19a	demi	200	0.320	0.520	60.090	490.440	1.450	59.380	0.130	31.030	b.d.	b.d.	272.330	184.220	2.500	0.730	0.560
10	T1	KB 103A 19a	demi	200	0.380	0.350	68.150	480.440	1.510	59.250	0.130	33.450	0.010	b.d.	272.980	163.590	2.970	0.780	0.570
10	T1	KB 103 A - 22	demi	25	0.170	0.840	8.560	94.900	1.290	10.790	0.070	3.080	b.d.	b.d.	46.250	b.d.	1.540	0.040	0.570
10	T1	KB 103 A - 22	demi	25	0.160	1.980	7.600	83.810	1.300	9.150	0.070	2.670	b.d.	b.d.	40.390	b.d.	1.450	0.030	0.590
10	T1	KB 103 A - 22	demi	50	0.190	1.070	12.200	138.300	1.300	14.000	0.080	4.790	b.d.	b.d.	65.820	b.d.	1.610	0.090	0.570
10	T1	KB 103 A - 22	demi	50	0.230	1.080	13.940	133.050	1.310	14.510	0.080	5.530	b.d.	b.d.	65.010	b.d.	1.650	0.120	0.570
10	T1	KB 103 A - 22	demi	200	0.300	0.670	51.090	469.510	1.480	36.060	0.110	25.210	0.110	b.d.	195.390	4.680	3.490	0.650	0.560
10	T1	KB 103 A - 22	demi	200	0.320	1.870	51.560	476.180	1.790	35.540	0.100	26.440	0.090	b.d.	194.240	6.490	3.010	0.640	1.590
10	T1	KB 103 A - 22	NaHCO3	25	0.190	1.290	10.730	89.220	1.350	11.670	0.070	5.530	b.d.	b.d.	217.610	b.d.	1.800	0.080	0.950
10	T1	KB 103 A - 22	NaHCO3	25	0.140	2.400	10.200	82.320	1.370	10.900	0.070	4.940	b.d.	b.d.	212.040	b.d.	1.760	0.070	0.360
10	T1	KB 103 A - 22	NaHCO3	50	0.210	2.110	17.280	143.820	1.470	16.900	0.080	8.120	b.d.	b.d.	229.570	b.d.	2.400	0.170	0.370
10	T1	KB 103 A - 22	NaHCO3	50	0.330	0.880	17.110	146.380	1.580	17.050	0.080	8.160	b.d.	b.d.	231.810	b.d.	2.140	0.170	0.380
10	T1	KB 103 A - 22	NaHCO3	200	0.340	0.940	55.200	473.460	1.380	41.700	0.110	26.340	0.020	b.d.	330.760	5.090	2.930	0.710	0.420
10	T1	KB 103 A - 22	NaHCO3	200	0.360	1.150	47.830	483.510	4.670	36.600	0.100	27.710	0.020	b.d.	341.230	4.980	3.120	0.710	0.460

dilution	Time	Sample Name	Solution	S/L g/mL	B mg/L	Ba mg/L	Ca mg/L	Cl mg/L	Fe mg/L	K mg/L	Li mg/L	Mg mg/L	Mn mg/L	Mo mg/L	Na mg/L	S mg/L	Si mg/L	Sr mg/L	Zn mg/L
10	T2	KB 101-14	NaHCO3	25	b.d.	1.090	10.330	99.370	0.890	16.610	0.060	3.180	b.d.	b.d.	234.240	0.000	1.690	0.020	0.090
10	T2	KB 101-14	NaHCO3	25	b.d.	1.250	9.710	102.440	0.880	13.520	0.060	2.950	b.d.	b.d.	234.680	0.000	1.500	0.020	0.080
10	T2	KB 101-14	NaHCO3	50	b.d.	1.310	16.160	154.100	0.970	25.650	0.070	6.120	b.d.	b.d.	262.460	20.210	2.170	0.110	0.120
10	T2	KB 101-14	NaHCO3	50	b.d.	1.320	18.630	136.340	0.930	24.030	0.080	6.760	b.d.	b.d.	260.280	20.150	2.440	0.130	0.080
10	T2	KB 101-14	NaHCO3	200	b.d.	1.010	54.480	440.520	1.640	55.830	0.110	25.160	b.d.	b.d.	417.500	20.570	5.460	0.620	0.110
10	T2	KB 101-14	NaHCO3	200	b.d.	0.710	60.410	454.600	1.270	61.460	0.110	27.260	b.d.	b.d.	435.700	24.110	5.380	0.690	0.110
10	T2	KB 103 A 01	NaHCO3	25	b.d.	1.850	3.890	52.570	12.670	12.190	0.070	3.680	b.d.	b.d.	239.570	b.d.	33.550	0.050	0.140
10	T2	KB 103 A 01	NaHCO3	25	b.d.	0.460	1.010	74.170	1.170	7.970	0.060	b.d.	b.d.	b.d.	249.420	b.d.	6.210	b.d.	0.090
10	T2	KB 103 A 01	NaHCO3	50	b.d.	1.120	5.790	66.810	27.590	20.970	0.090	8.280	b.d.	b.d.	264.940	b.d.	85.830	0.150	0.330
10	T2	KB 103 A 01	NaHCO3	50	b.d.	1.660	7.970	54.100	44.380	23.900	0.100	14.180	0.040	b.d.	264.850	b.d.	116.010	0.260	0.400
10	T2	KB 103 A 01	NaHCO3	200	b.d.	1.670	41.330	78.450	620.150	229.910	0.680	194.360	0.850	b.d.	459.030	58.210		1.460	1.130
10	T2	KB 103 A 01	NaHCO3	200	b.d.	0.370	6.390	186.920	20.310	19.400	0.070	5.790	b.d.	b.d.	417.210	56.060	99.620	0.080	0.250
10	T2	KB 103A 19b	NaHCO3	25	b.d.	1.030	9.190	96.410	0.920	14.730	0.060	3.290	b.d.	b.d.	225.900	0.000	2.270	0.030	0.110
10	T2	KB 103A 19b	NaHCO3	25	b.d.	0.630	9.100	69.850	0.900	15.080	0.070	3.140	b.d.	b.d.	217.430	0.000	2.030	0.020	0.070
10	T2	KB 103A 19b	NaHCO3	50	b.d.	0.470	12.700	138.530	0.910	23.500	0.070	5.360	b.d.	b.d.	229.800	0.000	2.430	0.080	0.070
10	T2	KB 103A 19b	NaHCO3	50	b.d.	0.800	46.500	126.380	1.200	33.090	0.070	16.140	b.d.	b.d.	252.720	0.000	3.030	0.470	0.200
10	T2	KB 103A 19b	NaHCO3	200	b.d.	1.080	42.390	412.460	1.280	39.640	0.100	19.950	b.d.	b.d.	326.070	0.000	3.850	0.510	0.100
10	T2	KB 103A 19b	NaHCO3	200	b.d.	0.860	44.030	434.010	1.280	40.320	0.100	20.880	b.d.	b.d.	331.680	0.000	3.880	0.530	0.100
10	T2	KB 103A 19a	NaHCO3	25	b.d.	1.090	8.180	82.510	0.880	16.170	0.070	2.930	b.d.	b.d.	217.370	0.000	1.660	0.020	0.070
10	T2	KB 103A 19a	NaHCO3	25	b.d.	0.490	8.800	79.530	0.880	19.920	0.070	3.190	b.d.	b.d.	216.500	0.000	1.610	0.020	0.080
10	T2	KB 103A 19a	NaHCO3	50	b.d.	2.030	13.530	118.260	1.110	18.910	0.070	5.180	b.d.	b.d.	227.840	0.000	2.650	0.080	0.150
10	T2	KB 103A 19a	NaHCO3	50	b.d.	1.440	13.710	126.390	0.930	19.380	0.070	5.370	b.d.	b.d.	229.960	0.000	2.430	0.090	0.130
10	T2	KB 103A 19a	NaHCO3	200	b.d.	1.390	43.860	392.850	1.880	36.690	0.100	20.850	0.020	b.d.	328.620	0.000	4.040	0.540	0.170
10	T2	KB 103A 19a	NaHCO3	200	b.d.	2.700	45.480	431.670	2.200	38.280	0.100	21.680	0.040	b.d.	333.490	0.000	4.140	0.550	0.610

dilution	Time	Sample Name	Solution	S/L g/mL	B mg/L	Ba mg/L	Ca mg/L	Cl mg/L	Fe mg/L	K mg/L	Li mg/L	Mg mg/L	Mn mg/L	Mo mg/L	Na mg/L	S mg/L	Si mg/L	Sr mg/L	Zn mg/L
10	T2	KB 101-14	demi	25	b.d.	1.240	7.680	90.600	1.210	15.940	0.050	2.890	b.d.	b.d.	51.890	16.730	1.410	0.030	0.140
10	T2	KB 101-14	demi	25	0.150	0.850	8.370	86.270	1.220	14.770	0.050	3.070	b.d.	b.d.	51.170	19.980	1.330	0.050	0.130
10	T2	KB 101-14	demi	50	0.090	1.050	16.440	139.060	1.220	24.050	0.060	6.740	b.d.	b.d.	87.980	38.550	1.670	0.140	0.110
10	T2	KB 101-14	demi	50	0.060	0.300	15.720	137.500	1.240	23.340	0.050	6.490	b.d.	b.d.	85.230	43.500	1.840	0.130	0.130
10	T2	KB 101-14	demi	200	0.210	13.600	66.920	480.410	4.390	58.760	0.100	32.770	b.d.	b.d.	279.010	184.080	3.690	1.030	0.170
10	T2	KB 101-14	demi	200	0.200	2.060	60.990	476.200	3.080	56.810	0.100	30.400	b.d.	b.d.	277.730	131.870	3.590	0.760	0.140
10	T2	KB 103A 19a	demi	25	b.d.	0.990	9.190	78.860	1.200	12.440	0.040	3.290	b.d.	b.d.	48.560	20.640	1.550	0.050	0.140
10	T2	KB 103A 19a	demi	25	b.d.	0.820	8.680	71.830	1.200	13.290	0.050	3.230	b.d.	b.d.	47.840	21.150	1.360	0.050	0.110
10	T2	KB 103A 19a	demi	50	0.050	1.050	17.950	144.540	1.240	22.580	0.060	7.320	b.d.	b.d.	90.220	47.960	1.970	0.170	0.130
10	T2	KB 103A 19a	demi	50	0.020	1.220	16.990	144.530	1.210	23.260	0.060	7.180	b.d.	b.d.	89.590	36.600	2.100	0.160	0.230
10	T2	KB 103A 19a	demi	200	0.190	7.190	62.420	512.680	1.580	59.320	0.100	31.250	b.d.	b.d.	289.210	105.880	3.570	0.860	0.140
10	T2	KB 103A 19a	demi	200	0.180	0.500	70.020	469.490	2.340	56.440	0.100	33.290	b.d.	b.d.	271.300	110.100	3.830	0.810	0.210
10	T2	KB 103 A - 22	demi	25	b.d.	0.840	9.070	91.990	1.210	9.190	0.050	2.560	b.d.	b.d.	45.450	b.d.	1.790	0.050	0.140
10	T2	KB 103 A - 22	demi	25	b.d.	1.030	8.010	81.100	1.210	7.110	0.050	2.080	b.d.	b.d.	41.040	b.d.	1.680	0.040	0.120
10	T2	KB 103 A - 22	demi	50	b.d.	0.380	13.270	129.950	1.200	12.830	0.050	4.470	b.d.	b.d.	62.990	b.d.	2.020	0.100	0.140
10	T2	KB 103 A - 22	demi	50	0.020	0.900	15.990	122.980	1.370	13.420	0.060	5.570	b.d.	b.d.	62.740	b.d.	2.440	0.140	0.140
10	T2	KB 103 A - 22	demi	200	0.140	1.150	99.080	471.670	19.680	43.330	0.080	40.640	0.230	b.d.	218.400	5.260	4.650	1.170	0.360
10	T2	KB 103 A - 22	demi	200	0.080	0.660	129.920	464.440	2.000	46.370	0.080	46.880	0.140	b.d.	217.410	5.390	2.720	1.400	0.180
10	T2	KB 103 A - 22	NaHCO3	25	b.d.	1.380	10.950	86.580	1.250	9.670	0.050	4.060	b.d.	b.d.	222.740	b.d.	2.250	0.090	0.190
10	T2	KB 103 A - 22	NaHCO3	25	b.d.	1.030	13.200	80.930	2.740	10.310	0.050	5.150	b.d.	b.d.	223.890	b.d.	2.480	0.120	0.330
10	T2	KB 103 A - 22	NaHCO3	50	0.020	0.610	23.350	127.090	3.990	16.990	0.050	9.080	b.d.	b.d.	234.550	b.d.	3.220	0.240	0.250
10	T2	KB 103 A - 22	NaHCO3	50	0.220	0.590	26.220	145.780	5.970	19.190	0.060	10.920	b.d.	b.d.	249.880	b.d.	3.590	0.290	0.370
10	T2	KB 103 A - 22	NaHCO3	200	0.210	1.440	60.570	462.850	1.810	40.090	0.080	24.490	0.040	b.d.	336.570	4.960	3.320	0.710	0.230
10	T2	KB 103 A - 22	NaHCO3	200	0.280	1.280	65.610	506.680	19.870	40.160	0.080	31.710	0.180	b.d.	364.560	b.d.	5.400	0.870	0.480

dilution	Time	Sample Name	Solution	S/L g/L	B mg/L	Ba mg/L	Ca mg/L	CI mg/L	Fe mg/L	K mg/L	Li mg/L	Mg mg/L	Mn mg/L	Mo mg/L	Na mg/L	S mg/L	Si mg/L	Sr mg/L	Zn mg/L
10	ТЗ	KB 101-14	NaHCO3	25	b.d.	1.610	9.380	89.590	0.880	21.620	0.070	3.370	b.d.	b.d.	236.210	b.d.	2.980	b.d.	0.090
10	Т3	KB 101-14	NaHCO3	25	b.d.	0.420	8.010	66.340	0.890	11.130	0.060	2.380	b.d.	b.d.	226.080	b.d.	2.220	b.d.	0.030
10	Т3	KB 101-14	NaHCO3	50	b.d.	0.810	13.860	132.620	0.970	19.860	0.070	5.430	b.d.	b.d.	256.440	b.d.	3.860	0.070	0.090
10	ТЗ	KB 101-14	NaHCO3	50	b.d.	0.710	15.860	132.280	0.970	19.950	0.070	5.730	b.d.	b.d.	252.820	b.d.	3.970	0.090	0.040
10	Т3	KB 101-14	NaHCO3	200	b.d.	1.120	52.070	427.510	1.970	48.790	0.110	23.940	b.d.	b.d.	419.030	b.d.	5.260	0.590	0.260
10	ТЗ	KB 101-14	NaHCO3	200	b.d.	1.030	59.010	429.510	2.520	52.290	0.110	26.700	b.d.	b.d.	422.580	b.d.	6.570	0.660	0.230
10	ТЗ	KB 103 A 01	NaHCO3	25	b.d.	0.610	1.410	34.300	1.230	6.700	0.060	b.d.	b.d.	b.d.	227.710	b.d.	4.610	b.d.	0.030
10	ТЗ	KB 103 A 01	NaHCO3	25	b.d.	0.480	1.250	40.320	1.220	6.520	0.060	b.d.	b.d.	b.d.	233.600	b.d.	4.740	b.d.	0.040
10	тз	KB 103 A 01	NaHCO3	50	b.d.	0.530	1.430	64.930	1.780	7.030	0.060	b.d.	b.d.	b.d.	237.770	b.d.	6.960	b.d.	0.060
10	тз	KB 103 A 01	NaHCO3	50	b.d.	0.740	0.810	72.140	1.820	6.380	0.060	b.d.	b.d.	b.d.	251.600	b.d.	7.710	b.d.	0.060
10	тз	KB 103 A 01	NaHCO3	200	b.d.	0.470	4.260	109.890	2.900	9.180	0.050	b.d.	b.d.	b.d.	372.680	56.070	47.730	0.030	0.080
		KB 103 A 01	NaHCO3	200															
10	Т3	KB 103A 19b	NaHCO3	25	b.d.	0.100	33.350	64.620	1.120	18.800	0.070	9.860	b.d.	b.d.	230.920	b.d.	2.810	0.260	0.030
10	Т3	KB 103A 19b	NaHCO3	25	b.d.	0.620	27.530	49.790	1.370	19.930	0.070	8.470	b.d.	b.d.	223.060	b.d.	2.740	0.210	0.110
10	Т3	KB 103A 19b	NaHCO3	50	b.d.	0.490	11.810	123.250	0.880	21.360	0.080	4.960	b.d.	b.d.	225.270	b.d.	2.380	0.060	0.040
10	Т3	KB 103A 19b	NaHCO3	50	b.d.	1.250	44.900	118.740	1.150	31.270	0.080	15.520	b.d.	b.d.	250.330	b.d.	3.030	0.450	0.200
10	Т3	KB 103A 19b	NaHCO3	200	b.d.	0.960	73.780	398.180	3.270	48.160	0.100	33.070	0.100	b.d.	350.020	b.d.	4.260	0.890	0.160
10	Т3	KB 103A 19b	NaHCO3	200	b.d.	1.170	75.090	397.970	3.020	48.650	0.110	34.590	0.090	b.d.	363.270	b.d.	4.230	0.930	0.140
10	Т3	KB 103A 19a	NaHCO3	25	b.d.	1.130	63.660	59.920	1.440	23.600	0.070	15.470	0.040	b.d.	238.060	b.d.	2.790	0.510	0.320
10	Т3	KB 103A 19a	NaHCO3	25	b.d.	0.640	91.670	66.340	10.920	31.590	0.070	24.390	0.250	b.d.	241.990	b.d.	4.820	0.700	0.340
10	Т3	KB 103A 19a	NaHCO3	50	b.d.	1.040	21.210	120.440	1.680	21.920	0.070	8.250	b.d.	b.d.	239.960	b.d.	3.450	0.190	0.110
10	Т3	KB 103A 19a	NaHCO3	50	b.d.	b.d.	20.330	121.100	b.d.	22.740	0.070	8.000	b.d.	b.d.	b.d.	b.d.	b.d.	0.180	0.110
10	Т3	KB 103A 19a	NaHCO3	200	b.d.	0.710	74.810	403.180	4.900	45.750	0.110	34.510	0.130	b.d.	364.200	b.d.	4.760	0.910	0.200
10	Т3	KB 103A 19a	NaHCO3	200	b.d.	0.550	76.170	439.460	3.960	44.960	0.100	34.730	0.120	b.d.	364.150	b.d.	4.200	0.930	0.090

dilution	Time	Sample Name	Solution	S/L g/L	B mg/L	Ba mg/L	Ca mg/L	CI mg/L	Fe mg/L	K mg/L	Li mg/L	Mg mg/L	Mn mg/L	Mo mg/L	Na mg/L	S mg/L	Si mg/L	Sr mg/L	Zn mg/L
10	ТЗ	KB 101-14	demi	25	0.220	0.630	8.790	91.390	1.050	16.590	b.d.	3.640	b.d.	b.d.	46.770	15.770	2.390	0.060	0.390
10	ТЗ	KB 101-14	demi	25	0.140	1.110	9.420	86.720	1.050	15.040	b.d.	3.860	b.d.	b.d.	47.360	17.960	2.510	0.070	0.410
10	ТЗ	KB 101-14	demi	50	0.190	1.120	18.240	147.230	1.080	23.200	b.d.	7.710	b.d.	b.d.	84.510	31.930	3.020	0.170	0.390
10	ТЗ	KB 101-14	demi	50	0.140	1.210	16.620	144.180	1.060	22.310	b.d.	7.110	b.d.	b.d.	83.470	33.300	2.850	0.160	0.380
10	Т3	KB 101-14	demi	200	0.350	1.130	57.310	484.380	1.030	49.660	0.090	28.120	b.d.	b.d.	268.840	b.d.	5.400	0.670	0.420
10	ТЗ	KB 101-14	demi	200	0.300	0.370	64.230	477.560	1.100	52.480	0.100	32.100	b.d.	b.d.	269.010	52.900	4.270	0.720	0.490
10	ТЗ	KB 103A 19a	demi	25	0.080	0.740	9.510	89.290	1.040	13.190	b.d.	3.720	b.d.	b.d.	48.810	18.240	2.360	0.060	0.410
10	Т3	KB 103A 19a	demi	25	b.d.	1.070	9.650	84.880	1.160	13.570	b.d.	3.980	b.d.	b.d.	48.040	17.660	2.740	0.080	0.390
10	ТЗ	KB 103A 19a	demi	50	0.110	0.430	18.550	146.210	1.140	21.900	b.d.	7.750	b.d.	b.d.	85.140	34.390	3.030	0.170	0.770
10	ТЗ	KB 103A 19a	demi	50	0.100	1.230	15.810	151.310	1.060	21.330	b.d.	7.100	b.d.	b.d.	85.830	15.600	3.610	0.150	0.390
10	Т3	KB 103A 19a	demi	200	0.240	2.870	56.520	492.930	1.060	50.620	0.090	28.360	b.d.	b.d.	275.160	0.000	4.610	0.650	0.520
10	ТЗ	KB 103A 19a	demi	200	0.220	1.140	64.470	477.850	1.080	48.960	0.090	30.540	b.d.	b.d.	268.520	7.670	4.730	0.720	0.470
10	Т3	KB 103 A - 22	demi	25	b.d.	0.670	9.550	97.300	1.030	12.480	b.d.	2.930	b.d.	b.d.	44.910	b.d.	2.420	0.070	0.400
10	ТЗ	KB 103 A - 22	demi	25	b.d.	2.580	8.740	86.310	1.050	9.170	b.d.	2.570	b.d.	b.d.	42.030	b.d.	2.420	0.070	0.480
10	ТЗ	KB 103 A - 22	demi	50	b.d.	1.010	14.300	139.960	1.040	15.080	b.d.	4.950	b.d.	b.d.	63.560	b.d.	2.690	0.130	0.430
10	ТЗ	KB 103 A - 22	demi	50	b.d.	1.200	16.530	133.580	1.060	15.340	b.d.	5.900	b.d.	b.d.	64.240	b.d.	3.200	0.160	0.480
10	ТЗ	KB 103 A - 22	demi	200	0.160	0.690	98.650	470.180	1.100	42.930	0.080	40.200	0.200	b.d.	212.630	b.d.	4.420	1.140	0.530
10	Т3	KB 103 A - 22	demi	200	0.140	1.090	129.300	464.060	1.120	45.940	0.080	47.560	0.150	b.d.	213.420	b.d.	3.490	1.430	0.540
10	Т3	KB 103 A - 22	NaHCO3	25	b.d.	1.220	15.340	90.940	1.110	13.320	b.d.	6.010	b.d.	b.d.	223.620	b.d.	3.410	0.150	0.500
10	Т3	KB 103 A - 22	NaHCO3	25	b.d.	0.750	12.610	84.180	1.060	12.060	b.d.	5.190	b.d.	b.d.	217.760	b.d.	3.150	0.120	0.440
10	ТЗ	KB 103 A - 22	NaHCO3	50	0.210	1.160	19.960	137.650	1.080	17.630	b.d.	8.070	b.d.	b.d.	235.450	b.d.	3.540	0.220	0.530
10	ТЗ	KB 103 A - 22	NaHCO3	50	0.180	1.250	22.460	148.190	1.130	18.960	b.d.	9.050	b.d.	b.d.	240.110	b.d.	3.720	0.240	0.560
10	ТЗ	KB 103 A - 22	NaHCO3	200	0.240	1.420	57.740	467.870	1.110	42.150	0.080	26.010	0.020	b.d.	342.210	b.d.	3.990	0.730	0.610
10	ТЗ	KB 103 A - 22	NaHCO3	200	0.210	2.440	59.290	491.360	1.110	39.360	0.080	28.320	0.110	b.d.	347.180	b.d.	4.630	0.760	0.520

REV 0 Boring KB-102 PROJECT: 104472 KCB2 CLIENT: DELTA ENERGY B.V.	ı										
していたいのです。         していたいのです。         COORDINATES           1	ISCS MBOL	2		E		REV 0 Boring KB-103A CLIENT: D4472 KCB2 CLIENT: DELTA ENERGY B.V.		N (su	vo.	LE CC	
HORIZONIAL DATUM: RD New VERTICAL DATUM: NAP <u>HORIZONIAL DATUM: RD New</u> VERTICAL DATUM: NAP <u>DESCRIPTION</u> <u>65.0</u>	-26	EVATIO Meters)	Meters) AMPLE OR UN NO.	0W/150	R %REC	N. 384743.07 m E. 39212.26 m GROUND SURFACE ELEVATION: 4.76 m HORIZONTAL DATUM: RN New VERTICAL DATUM: NAP	USCS	ELEVA1 (Mete	SAMP SAMP OR ND	BLOW/1 & (P OR %I PROF	
R42 R5.5 R6.5 R6.5 R6.5 R6.5 R6.5 R6.5 R6.5		-65.5	R-42	<u>* 금 (</u> 2 1009	• •	DESCRIPTION	sp	-65.5 -	R-42	100%	
-66.0     71.0     R-43     100%       -66.5     71.5		-66.0 -66.5 71. -66.5	.0 R-43	3 1009		70.48-72.0 m Fat clay, (ch), 90% fines, high plasticity, no dilatancy, high toughness; 10% sand, fine, rounded, spherical, soft hardness; dark greenish gray (SGY 4/1) to dark greenish gray (SG 4/1), dry, weak HCl reaction, very stiff consistency, weak cementation, little mica, upper 30 cm is a mix of clay and overlying black sand (Marine).	ch	-66.0 7	1.0 R-43 /1.5	100%	
-67.5 72.5 R-44 100% C-101	sp	-67.0 - 72 -67.5 -	.0 ST-2	2 1009		72.0-72.5 m Sandy fat clay, (ch), 70% fines, medium plasticity, slow dilatancy, medium toughness; 30% sand, fine, rounded, spherical, medium hardness; dark greenish gray (5GY 4/1) and dark greenish gray (5G 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, gradual transition with adjacent lithologies (Marine).	ch	-67.5	2.0		
-68.0 73.0 R-45 100%		-68.0 -68.5 -68.5	.0 - R-44	4 1009		72.5-73.55 m Fat clay, (ch), 95% fines, high plasticity, no dilatancy, high toughness; 5% sand, fine, rounded, spherical, soft hardness; dark greenish gray (SGY 4/1) to dark greenish gray (SG 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, (Marine).	ch	-68.0 7 -68.5	3.0 73.5	100%	
-69.0 74.0 R.46 100% 100% 100%		-69.0 -69.5	.5- 	5 1009		73.55-74.58 m Fat clay with sand, (ch), 75% fines, medium plasticity, slow dilatancy, medium toughness; 25% sand, fine, rounded, spherical, medium hardness; dark greenish gray (SGY 4/1) and dark greenish gray (SG 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, gradual transition with adjacent lithologies (Marine).	ch	-69.0 - 7 -69.5 - ;	4.0 74.5	100%	
-70.0     75.0     100%       77.0     R-47       100%     74.73-77.4 m Fat clay, (ch), 90% fines, high plasticity, no dilatancy, high toughness; 10% sand, fine, rounded, spherical, soft hardness; dark greenish gray (SGY 4/1), dry, weak HCI reaction, very stiff consistency, little mica,		-70.0 75	.5- 	1009		74.58-75.0 m Fat clay, (ch), 90% fines, high plasticity, no dilatancy, high toughness; 10% sand, fine, rounded, spherical, soft hardness; dark greenish gray (SGY 4/1) to dark greenish gray (SG 4/1), dry, weak HCI reaction, very stiff consistency, weak cemen- tation, little mica, trace glauconite, gradual transition to adjacent lithologies (Marine).	ch	-70.0	R-47	98%	
-70.5 75.5 (Marine).	ch	-70.5 -71.0 75.	.5- ST-5	5 1009		75.0-76.0 m Fat clay with sand, (ch), 85% fines, high plasticity, slow dilatancy, medium toughness; 15% sand, fine, rounded, spherical, medium hardness; dark greenish gray (5GY 4/1) and dark greenish gray (5G 4/1), dry, weak HCl reaction, very stiff consistency, weak cementation, little mica, little glauconite, gradual transition with adjacent lithologies, sand content varies from 10-25% (Marine).	ch	-70.5 7	5.5 ST-3	100%	
-71.5         76.5         5T-3         100%           -72.0         77.0         77.4-77.75 m Silty clayey sand, (sc-sm), 60% sand, fine, rounded, spherical, medium hardness; 40% fines, medium		-71.5 76	.5 R-46	6 1009	6	76.0-76.33 m Fat clay, (ch), 95% fines, high plasticity, no dilatancy, high toughness; 5% sand, fine, rounded, spherical, soft hardness; dark greenish gray (SGY 4/1) to dark greenish gray (SG 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, little glauconite, (Marine). 76.32-76 78 m Silty clause sand (sc-sm) 60% sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fines, medium, and the sand fine rounded spherical medium hardness; 40% fine sand fine rounded spherical me	ch	-71.5 - 7	6.5 R-48	100%	
-72.5     77.5     R-48     100%     plasticity, rapid dilatancy, low toughness; dark greenish gray (5GY 4/1), dry, weak HCI reaction, weak cementation, little mica, (Marine).       -72.5     77.5     77.5     77.7-98 m Sandy fat clay, (ch), 70% fines, medium plasticity, low toughness; 30% sand, fine, rounded,	sc- sm	-72.5	-			plasticity, rapid dilatancy, low toughness; dark greenish gray (SGY 4/1), moist, weak HCl reaction, weak cementation, little mica, some glauconite, gradual transition to adjacet lithologies (Marine). 76.78-77.19 m Fat clay, (ch), 90% fines, high plasticity, no dilatancy, high toughness; 10% sand, fine, rounded,	ch sc-	-72.5	/7.5 R-49	100%	
-73.0 78.0 R-49 100% Re49 100% 77.98-80.04 m Fat clay, (ch), 90% fines, high plasticity, no dilatancy, high	cn	-73.0	.0 R-47	7 1009		spherical, soft hardness; dark greenish gray (5GY 4/1) to dark greenish gray (5G 4/1), dry, weak HCl reaction, very stiff consistency, weak cementation, little mica, some glauconite, (Marine). 77.19-77.87 m Silty clayey sand, (sc-sm), 60% sand, fine, rounded, spherical, medium hardness; 40% fines, medium	sm	-73.0 - 7	8.0		
-73.5     -74.0     79.0     5T-4     100%     str.4     100%     str.4	ch	-73.5 - 78	.5 ST-6	5 1009		plasticity, rapid dilatancy, low toughness; dark greenish gray (5GY 4/1), moist, weak HCI reaction, weak cementation, little mica, some glauconite, gradual transition to underlying lithology (Marine).		-74.0	8.5 K-50		
-74.5 79.5 ST-5 100% -75.0 R-50 100% 80.04-80.4 m Silty clayey sand, (sc-sm), 60% sand, fine, rounded, spherical, medium hardness; 40% fines, medium plasticity, rapid dilatancy, low toughness; dark greenish gray (5GY 4/1), dry, weak HCl reaction, weak cementation, little mica, gradual transition to adjacent lithologies (Marine).	sc- sm	-74.5 -75.0 80	.0 - ST-7 	7 1009 B 1009		77.87-80.6 m Fat clay, (ch), 95% fines, high plasticity, no dilatancy, high toughness; 5% sand, fine, rounded, spherical, soft hardness; dark greenish gray (SGY 4/1) to dark greenish gray (SG 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, trace glauconite, (Marine).	ch	-74.5 7	9.5 ST-6 R-51	100%	
<ul> <li>-75.5</li> <li>-75.5</li> <li>-76.0</li> <li>81.0</li> <li>-8.51</li> <li>43%</li> <li>43%</li> <li>80.4-81.13 m Fat clay, (ch), 90% fines, high plasticity, no dilatancy, high toughness; 10% sand, fine, rounded, spherical, soft hardness; dark greenish gray (5GY 4/1), dry, weak HCI reaction, very stiff consistency, little mica, gradual transition to adjacent lithologies (Marine).</li> </ul>	ch	-75.5 -76.0 81	.5 R-49	9 1009		80.6-80.83 m Silty clayey sand, (sc-sm), 70% sand; 30% fines, medium plasticity, rapid dilatancy, low toughness; dark greenish gray (5GY 4/1) and dark greenish gray (5G 4/1), moist, strong HCI reaction, weak cementation, little mica, little glauconite, gradual transition to underlying lithology (Marine).	sc- sm	-76.0 {	0.5 R-51	63%	
-76.5       81.5         -77.0       82.0         -77.0       82.0         R-52       100%         R52       100%	ch	-76.5 - 81	.5 R-50	0 1009		80.83-82.58 m Fat clay, (ch), 95% fines, high plasticity, no dilatancy, high toughness; 5% sand, fine, rounded, spherical, soft hardness; dark greenish gray (5GY 4/1) to dark greenish gray (5G 4/1), dry, weak HCl reaction, very stiff consistency, weak cementation, little mica, trace glauconite, (Marine).	ch	-76.5 8	1.5 R-52	95%	
		-77.5	.5-	1 1000		82.58-82.75 m Silty clayey sand, (sc-sm), 70% sand, fine, rounded, spherical, me- dium hardness; 30% fines, medium plasticity, rapid dilatancy, low toughness; dark greenish gray (SGY 4/1) and dark greenish gray (SG 4/1), moist, strong HCI reaction, weak cemen- tation, little mica, little glauconite, gradual transition to underlying lithology (Marine).	SC-	-77.5 8	2.5 R-53	100%	
-78.5 -79.5 -70.5 -70.5		-78.5	.0	1 1007		82.75-83.25 m Fat clay with sand, (ch), 85% fines, high plasticity, no dilatancy, high toughness; 15% sand, fine, rounded, spherical, soft hardness; dark greenish gray (5G 4/1) to dark greenish gray (5G 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, trace glauconite, gradual transition to adjacent lithologies (Marine). 83.25-83.83 m Silty clayer sand (sc-sm) 70% sand fine rounded spherical medium hardness; 30% fines, medium	ch	-78.5	3.0 83.5 R-54	100%	
-79.0 84.0 R-54 100% graduline, lace, large > 2 cli sien nagments.	sc- sm	-79.0	R-52	2 1009		plasticity, rapid dilatanoy, low toughness; dark greenish gray (5GY 4/1) and dark greenish gray (5G 4/1), moist, strong HCI reaction, weak cementation, little mica, little glauconite, gradual transition to underlying lithology, some pockets of 100% sand (Marine).	sm	-79.0 8	4.0		
79.5 100% 111		-79.5 - 84	.5 ST-8	3 1009		83.83-84.5 m Fat clay with sand, (ch), 85% fines, high plasticity, no dilatancy, high toughness; 15% sand, fine, rounded, spherical, soft hardness; dark greenish gray (SGY 4/1) to dark greenish gray (SG 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, trace glauconite, gradual transition to adjacent lithologies (Marine).		-79.5 - 8	4.5 R-55 R-56	100%	
DATE/TIME STARTED: 27 June 2011 / 13:00 DRILLING METHOD: SMET Soil Coring - 240 mm borehole, 100 mm core sample borekite anoundwater a vicrostifier	local	-80.5 -80.5 -81.0 85	.0 ST-9 .5 R-53	9 1009 3 1009	6	84.5-88.0 m Silty clayey sand, (sc-sm), 70% sand, fine to medium, subrounded, spherical; 30% fines, medium					
CHECKED BY: Erich Zom FIELD GEOLOGIST: DARKOR, EVZIJML DATE/TIME FINISHED: 29 June 2011 / 10:00  DRILLING CO. BMNED/SMET DRILL RIG: Fraste FS300 (SMET ID: GFR2) HAMMER ID: NA APPROVED BY: Mark Zatezalo  DRILLER: Bart Caers, Nicholas Meeus UNECRO D S M M D S M	odified ind, nder-	-81.5 - 86	.5 	4 1009		plasticity; grayish olive green (SGY 3/2), moist, weak HCI reaction, homogeneous, trace Glauconite grains, becoming sandier with depth, 80/20 to 90/10, sand with clay.	sc- sm				
recurrence): Reginaira van Reeur, Bart Horemans, Joelle Guisand, Danny Dresen doudy, rain, 10-20° C.		-82.5 -83.0	.5 - - - - - - - - - - - - - - - - - - -	5 1009							
		-83.5 -84.0	.0 - .5 - R-56	6 1009	6	88.0-97.43 m Poorly graded sand, (sp), 95% sand, fine to medium, subrounded, spherical; 5% fines; dark greenish gray (SGY 4/1) to grayish olive green (SGY 3/2), moist, weak HCl reaction, homogeneous, trace Glauconite grains, trace mica, fines content increasing with depth, to SP-SC.					
		-84.5	.0 .5 R-57	7 1009	6		sp				
		-85.0 - 90	.0								
		-86.0		00%	10						

REV 0 Boring KB-104 PROJECT: 104472 KCE CLIENT: DELTA ENERGY	82 B.V.
COORDINATES N. 384596.32 m E. 39364.80 m GROUND SURFACE ELEVATION: 4.93 m HORIZONTAL DATUM: RD New VERTICAL DATUM: NAP	USCS SYMBOL
3254-74.71 m Poorly graded sand, (sp), 95% sand, fine to medium, subrounded, spherical, medium hardness; 5% fines; greenish black (5GY 2/1) to greenish black (5G 2/1), moist, weak HCI reaction, homogeneous, with glauconite, sand is 60-70% glauconite, 25-35% quartz and up to 5% carbonate, and smears of light, olive gray (SY 5/2) due to higher quarttz and clay content, becoming more saturated with depth closer to boom clay (Marine).	sp
74.71-76.81 m Fat clay, (ch), 95% fines, high plasticity, no dilatancy, high toughness; 5% sand, fine, subrounded, spherical; dark gray (N3) to dark greenish gray (5GY 4/1), dry, weak HCl reaction, mottled, very stiff consistency, weak cementation.	ch
76.81-77.91 m Fat clay with sand, (ch), 80% fines, high plasticity, no dilatancy, high toughness; 20% sand, fine, subrounded, spherical; dark gray (N3) to dark greenish gray (5GY 4/1), dry, weak HCl reaction, very stiff consistency, weak cementation.	ch
77.91-79.7 m Fat clay, (ch), 95% fines, high plasticity, high dry strength, no dilatancy, high toughness; 5% sand, fine, subrounded, spherical; dark gray (N3) to dark greenish gray (SGY 4/1), dry, weak HCl reaction, mottled, very stiff consistency, weak cementation.	, ch
79.7-80.92 m Fat clay with sand, (ch), 85% fines, high plasticity, high dry strength, no dilatancy, high toughness; 15% sand, fine, subrounded, spherical, medium hardness; dark greenish gray (5G 4/1) to dark greenish gray (5GY 4/1), dry weak HCl reaction, very stiff consistency, weak cementation, little mica, (Marine).	6 y, ch
80.92-81.7 m Fat clay, (ch), 95% fines, high plasticity, no dilatancy, high toughness; 5% sand, fine, subrounded, spherical, medium hardness; dark greenish gray (5G 4/1) to dark greenish gray (5GY 4/1), dry, weak HCl reaction, mottled, very stiff consistency, weak cementation, trace mica, (Marine).	ch
81.7-82.52 m Sandy fat clay, (ch), 70% fines, high plasticity, no dilatancy, high tough- ness; 30% sand, fine to mediuu subrounded, spherical, medium hardness; dark greenish gray (5G 4/1) to dark greenish gray (5GY 4/1), dry, weak HC reaction, very stiff consis- tency, weak cementation, little mica, gradual transition to adjacent lithologies (Marine).	m, I <sub>ch</sub>
82.52-83.28 m Silty clayey sand, (sc-sm), 75% sand, fine to medium, subrounded, spherical, medium hardness; 25% fines, low plasticity, slow dilatancy, low toughness; dark greenish gray (SG 4/1), moist, weak HCl reaction, homogeneous, with glauconite, (Marine).	sc- sm
33.28-83.58 m Fat clay with sand, (ch), 75% fines, high plasticity, no dilatancy, high toughness; 25% sand, fine, subrounded, spherical, medium hardness; dark greenish gray (SGY 4/1), dry, strong HCI reaction, very stiff consistency, weak cementation, little mica, gradual transition to adjacent lithologies (Marine).	ch sc-
83.58-83.9 m Silty clayey sand, (sc-sm), 75% sand, fine to medium, subrounded, spherical, medium hardness; 25% fines, low plasticity, slow dilatancy, low toughness; dark greenish gray (SG 4/1), moist, weak HCI reaction, homogeneous, very stiff consistency, with glauconite, (Marine).	sm
83.9-85.35 m Poorty graded sand, (sp), 95% sand, fine to medium, subrounded, sphe- rical, medium hardness; 5% fir dark greenish gray (SGY 4/1) and greenish black (SGY 2/1), moist, weak HCI reaction, homogeneous, with glauconite glauconite is fine grained sand making up 20-25% of sand, remainder is quartz with minor carbonate (Marine).	nes; <sup>sp</sup> e,

	REV 0 Boring KB-105A PROJECT: 104472 KCB2 CLIENT: DELTA ENERGY B.V.		REV 0 Boring KB-101 PROJECT: 104472 KCB	2					
EVATION Meters) DEPTH Meters) OR OR OR NON N SAMPLE OR OR N N SAMPLE OR OR POFILE	COURDINALS N. 384396.32 m E. 38812.79 m GRUND SURFACE ELEVATION: 5.02 m GRUND SURFACE ELEVATION: 5.02 m GRUND SURFACE ELEVATION: SOL TO SUBJECT	ATION eters) eters) MPLE NN NN W(15cm V(15cm V(15cm V(15cm OFLE	COORDINATES N. 384585.88 m E. 39058.54 m GROUND SURACE ELEVATION: 4.90 m	SCS MBOL					
III         III         IIII         IIIII         IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII	DESCRIPTION 33.33-68.45 m Poorly graded sand, (sp), 95% sand, fine to medium, well rounded, spherical, medium hardness; 5% fines, low plasticity; dusky green (5G 3/2) and greenish black (5G 2/1), moist, weak HCI reaction, homogeneous, little 5 to 20 mm brown sand lenses, sand is about 50% quartz, 50% glauconite, less than 5% carbonate grains, soil has plasticity despite very low fines content (Marine). sp	Image: Section 1         Image: Section 1 <th 1<<="" image:="" section="" td=""><td>HORIZONTAL DATUM: DD New VERTICAL DATUM: NAP DESCRIPTION 58.0-69.03 m Poorly graded sand, (sp), 95% sand, fine to medium, subrounded, spherical, medium hardness; 5% fines; greenish black (SG 2/1) to greenish black (SGY 2/1), moist, weak HCI reaction, homogeneous, with glauconite, sand is approximately 50% glauconite and 50% quartz, glauconite is fine grained sized sand (Marine).</td><td>sp</td><td></td><td></td><td></td><td></td></th>	<td>HORIZONTAL DATUM: DD New VERTICAL DATUM: NAP DESCRIPTION 58.0-69.03 m Poorly graded sand, (sp), 95% sand, fine to medium, subrounded, spherical, medium hardness; 5% fines; greenish black (SG 2/1) to greenish black (SGY 2/1), moist, weak HCI reaction, homogeneous, with glauconite, sand is approximately 50% glauconite and 50% quartz, glauconite is fine grained sized sand (Marine).</td> <td>sp</td> <td></td> <td></td> <td></td> <td></td>	HORIZONTAL DATUM: DD New VERTICAL DATUM: NAP DESCRIPTION 58.0-69.03 m Poorly graded sand, (sp), 95% sand, fine to medium, subrounded, spherical, medium hardness; 5% fines; greenish black (SG 2/1) to greenish black (SGY 2/1), moist, weak HCI reaction, homogeneous, with glauconite, sand is approximately 50% glauconite and 50% quartz, glauconite is fine grained sized sand (Marine).	sp				
-63.0     68.0       -63.5     68.5       -64.0     69.0       -64.5     69.5       -65.0     70.0       -65.5     70.5       -66.0     71.0       R-44     100%	<ul> <li>68.45-72.67 m Fat clay, (ch), 95% fines, high plasticity, no dilatancy, high toughness; 5% sand, fine, rounded, spherical, soft hardness; dark greenish gray (5GY 4/1), dry, weak HCl reaction, very stiff consistency, little mica, (Marine).</li> <li>68.45-72.67 m Fat clay, (ch), 95% fines, high plasticity, no dilatancy, high toughness; 5% sand, fine, rounded, spherical, soft hardness; dark greenish gray (5GY 4/1), dry, weak HCl reaction, very stiff consistency, little mica, (Marine).</li> </ul>	-62.5         67.5           -63.0         68.0           -63.5         68.5           -64.0         69.0           -64.5         69.5           -65.5         70.0           -65.5         70.5           -66.0         70.0	<ul> <li>69.03-69.44 m Fat clay, (ch), 90% fines, medium plasticity, no dilatancy, high toughness; 10% sand, fine, rounded, spherical, soft hardness; dark greenish gray (SGY 4/1) to dark greenish gray (SG 4/1), dry, strong HCI reaction, very stiff consistency, weak cementation, little mica, some glauconite, (Marine).</li> <li>69.44-69.92 m Clayey sand, (sc), 70% sand, fine, rounded, spherical, medium hardness; 30% fines, medium plasticity, rapid dilatancy, low toughness; dark greenish gray (SGY 4/1) and dark greenish gray (SG 4/1), moist, strong HCI reaction, weak cementation, little mica, little glauconite, gradual transition to underlying lithology (Marine).</li> <li>69.92-70.67 m Fat clay, (ch), 95% fines, high plasticity, no dilatancy, high toughness; 5% sand, fine, rounded, spherical, soft hardness; dark greenish gray (SGY 4/1) to dark greenish gray (SG 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, little glauconite, (Marine).</li> <li>70.67-71.26 m Clayey sand, (sc), 80% sand, fine, rounded, spherical, medium hardness; 20% fines, medium</li> </ul>	dn sc f dn	Number of the second se	ON NOT 314WS 808 808 808 808 808 808 808 808 808 80	% OR %ÄEC PROFILE	70.48-7	
-66.5     71.5       -67.0     72.0       -67.5     72.5       -68.0     73.0       -68.5     73.5       -69.0     74.0       -69.5     74.5	72.67-73.18 m Sandy fat clay, (ch), 50% sand, fine, rounded, spherical, soft hardness; 50% fines, medium plasticity, no dilatancy, medium toughness; dark greenish gray (SGY 4/1), dry, weak HCI reaction, very stiff consistency, gradual transition to adjacent lithologies (Marine).       ch         73.18-73.71 m Fat clay, (ch), 95% fines, high plasticity, no dilatancy, high toughness; 5% sand, fine, rounded, spherical, soft hardness; 5% sand, fine, rounded, spherical, soft hardness; dark greenish gray (SGY 4/1), dry, weak HCI reaction, very stiff consistency, little mica, gradual transition to adjacent lithologies (Marine).       ch         73.71-74.28 m Sandy fat clay, (ch), 50% sand, fine, rounded, spherical, soft hardness; 50% fines, medium plasticity, no dilatancy, medium toughness; dark greenish gray (SGY 4/1), dry, weak HCI reaction, very stiff consistency, gradual transition to adjacent lithologies (Marine).       ch         ransition to adjacent lithologies (Marine).       ch       ch	66.5         71.0         71.0           66.5         71.5         8.71           67.0         72.0         8.71           68.0         73.0         51.2           68.0         73.0         51.3           69.0         74.0         8.72           69.5         74.5         9.6	<ul> <li>plasticity, rapid dilatancy, low toughness; dark greenish gray (5GY 4/1) and dark greenish gray (5G 4/1), moist, strong HCI reaction, homogeneous, weak cementation, little mica, little glauconite, gradual transition to adjacent lithologies (Marine).</li> <li>71.26-72.0 m Fat clay, (ch), 90% fines, high plasticity, no dilatancy, high toughness; 10% sand, fine, rounded, spherical, soft hardness; dark greenish gray (5GY 4/1) to dark greenish gray (5G 4/1), dry, strong HCI reaction, very stiff consistency, weak cementation, little mica, some glauconite, (Marine).</li> <li>72.0-74.9 m Fat clay, uth sand, (ch), 80% fines, medium plasticity, no dilatancy, high toughness; 20% sand, fine, rounded, spherical, dark greenish gray (5G 4/1) to dark greenish gray (5G 4/1), dry, strong HCI reaction, very stiff consistency, weak cementation, little mica, some glauconite, (Marine).</li> </ul>	sc dh dh	-66.5 -71.0 -67.0 -67.5 -67.0 -67.5 -72.0 -68.0 -73.0 -68.5 -73.0 -68.5 -73.0 -69.0 -74.0 -69.5 -74.0	R-43 100' 5 ST-2 100 5 ST-3 100 7 R-44 100 7 R-44 100 7 R-45 100		spherica stiff cor 72.0-72. rounder reaction 72.5-73. soft hai consisti 73.55-7; fine, ro HCI rea (Mariny 74.58-7;	
-70.0 75.0 R-48 100% -70.5 75.5 -71.0 76.0 R-49 99% -71.5 76.5	74.28-76.28 m Fat clay, (ch), 100% fines, high plasticity, no dilatancy, high toughness; dark greenish gray (5GY 4/1) and dark greenish gray (5G 4/1), dry, weak HCI reaction, very stiff consistency, little mica, trace sand, gradual transition to adjacent lithologies (Marine).       h         76.28-77.16 m Silty clayey sand, (sc-sm), 75% sand, fine, rounded, spherical, soft hardness; 25% fines, medium plasticity, slow dilatancy, medium toughness; dark greenish gray (5G 4/1), dry, weak       sc-	-70.0 -70.5 -71.5 -71.5 76.0 -71.5 76.5 51-4 100%	74.9-76.5 m Clayey sand, (sc), 80% sand, fine, subrounded, spherical; 20% fines; grayish olive green (5GY 3/2) to dark greenish gray (5GY 4/1), dry, weak HCI reaction, homogeneous, little glauconite, fines content fluctuates +\- 10%, more firm and cohesive in some spots, more crumbly and sandy in other spots.	sc	-70.0 75.0 -70.5 -71.0 76.0 -71.5 76.5 76.5	ST-4 100' ST-5 100 ST-5 100 ST-5 100		spherica consiste 75.0-76. rounde reaction litholog 76.0-76. spheric	
-72.0         77.0         R-50         91%           -72.5         77.5         ST-4         100%           -73.0         78.0         R-51         100%           -73.5         78.5         R-51         100%           -74.0         79.0         R-52         100%	HCI reaction, homogeneous, gradual transition to adjacent lithologies (Marine).       sm         77.16-77.8 m Fat clay, (ch), 95% fines, high plasticity, no dilatancy, high toughness; 5% sand, fine, rounded, spherical, soft hardness; dark greenish gray (SGY 4/1) and dark greenish gray (SG 4/1), dry, weak HCI reaction, very stiff consistency, little mica, gradual transition toadjacent lithologies (Marine).         77.8-78.89 m Poorly graded sand with silt, (sp-sm), 90% sand, fine, rounded, spherical, soft hardness; 10% fines, medium plasticity, low dilatancy, low toughness; dark greenish gray (SGY 4/1) and dark greenish gray (SG 4/1), moist, strong HCI reaction, homogeneous, trace mica, and glauconite, (Marine).         78.89-79.65 m Sandy fat clay, (ch), 50% sand, fine, rounded, spherical, soft hardness; 50% fines, medium plasticity, no dilatancy, medium toughness; dark greenish gray (SGY 4/1), moist, weak HCI reaction, stiff consistency, little mica, ch	-72.0 77.0 -72.5 77.5 R-75 95% -73.0 78.0 -73.5 78.5 R-76 100% -74.0 79.0	<ul> <li>76.5-78.36 m Fat clay, (ch), 90% fines, high plasticity, no dilatancy, high toughness; 10% sand, fine, rounded, spherical, soft hardness; grayish olive green (SGY 3/2) to dark greenish gray (SG 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, trace mica, some glauconite, (Marine).</li> <li>78.36-78.71 m Clayey sand, (sc), 80% sand, fine, subrounded, spherical; 20% fines; grayish olive green (SGY 3/2) to dark greenish gray (SGY 4/1), dry, weak HCI reaction, homogeneous, little glauconite.</li> <li>78.71-78.98 m Fat clay, (ch), 90% fines, high plasticity, no dilatancy, high toughness; 10% sand, fine, rounded, spherical, soft hardness; grayish olive green (SGY 3/2) to dark greenish gray (SG 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, trace mica, some glauconite, (Marine).</li> </ul>	ch sc ch	-72.0 77.0 77.5 77.5 77.0 78.0 78.0 78.0 78.5 78.5 74.0 79.0	R-46 100 R-47 100 F ST-6 100 ST-7 100		stiff con 76.33-70 plastici cement 76.78-7 spheric stiff con 77.19-7 plastici	
-74.5 79.5 R-53 100%	percent of sand vs fines changes on cm scale, common glauconite sand grains (Marine).	-74.5         79.5         R-77         100%           -75.0         R-78	<ul> <li>78.98-79.08 m Clayey sand, (sc), 80% sand, fine, subrounded, spherical; 20% fines; grayish olive green (SGY 3/2) to dark greenish gray (SGY 4/1), dry, weak HCI reaction, homogeneous, little glauconite.</li> <li>79.08-80.06 m Fat clay, (ch), 90% fines, high plasticity, no dilatancy, high toughness; 10% sand, fine, rounded, spherical, soft hardness; grayish olive green (SGY 3/2) to dark greenish gray (SG 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, trace mica, some glauconite, (Marine).</li> <li>80.06-85.0 m Clayey sand, (sc), 85% sand, fine, subrounded, spherical; 15% fines; grayish olive green (SGY 3/2) to dark greenish gray (SGY 4/1), dry, weak HCI reaction, homogeneous, some glauconite.</li> </ul>	/ ch	-74.5 79.5 -75.0 80.0 -75.5 -76.0 81.0 -76.5 81.5	R-48 100' R-48 100' R-49 100 R-49 100	s	77.87-84 soft hat consiste 80.6-80. greenis little gl 80.83-82 spheric	
		-77.0 82.0 -77.5 82.5 R-80 100% -78.0 83.0 -78.5 83.5 -79.0 84.0 -79.0 84.0 -79.0 84.0 -79.0 84.0		sc	-77.0 82.0 -77.5 -78.0 83.0 -78.5 83.5 -79.0 84.0	R-50 100 R-51 100 R-51 100 R-52 100 D	%	82.75-83 rounde reaction	
		-79.5 84.5 80.0 R-83 100%			-79.5 -80.0 -80.5 -80.5 -80.5 -80.5 -81.0 -81.5 -81.5 -81.0 -81.5 -81.5 -81.0 -81.5 -81.5 -81.0 -81.5 -81.5 -80.0 -80.5 -80.0	ST-9 100 ; R-53 100 5	96	83.25-83 plasticit strong k some p 83.83-84 rounde reaction litholoc 84.5-88 plastici	
					-82.0 -82.5 87.0 -83.0 -83.5 -83.0 88.0 -83.5 88.5 -84.0	R-54 100' R-55 100 R-55 100 R-56 100	96	88.0-97. gray (5 trace m	
					-84.5 -85.0 -85.5 -85.0 90.0 -85.5 90.5 -86.0	R-57 100 R-58 100	%		

		REV 0 Boring KB-103A PROJECT: 104472 KCB2 CLIENT: DELTA ENERGY B.V	
		COORDINATES N. 384743.07 m E. 39212.26 m GROUND SURFACE ELEVATION: 4.76 m HORIZONTAL DATUM: RD New VERTICAL DATUM: NAP	USCS
:		DESCRIPTION	sn
	Γ	70.48-72.0 m Fat clay, (ch), 90% fines, high plasticity, no dilatancy, high toughness; 10% sand, fine, rounded, spherical, soft hardness; dark greenish gray (SGY 4/1) to dark greenish gray (SG 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, upper 30 cm is a mix of clay and overlying black sand (Marine). 72.0-72.5 m Sandy fat clay, (ch), 70% fines, medium plasticity, slow dilatancy, medium toughness; 30% sand, fine,	ch
	]	rounded, spherical, medium hardness; dark greenish gray (5GY 4/1) and dark greenish gray (5G 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, gradual transition with adjacent lithologies (Marine).	ch
		72.5-73.55 m Fat clay, (ch), 95% fines, high plasticity, no dilatancy, high toughness; 5% sand, fine, rounded, spherical, soft hardness; dark greenish gray (SGY 4/1) to dark greenish gray (SG 4/1), dry, weak HCl reaction, very stiff consistency, weak cementation, little mica, (Marine).	ch
		73.55-74.58 m Fat clay with sand, (ch), 75% fines, medium plasticity, slow dilatancy, medium toughness; 25% sand, fine, rounded, spherical, medium hardness; dark greenish gray (5GY 4/1) and dark greenish gray (5G 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, gradual transition with adjacent lithologies (Marine).	ch
		74.58-75.0 m Fat clay, (ch), 90% fines, high plasticity, no dilatancy, high toughness; 10% sand, fine, rounded, spherical, soft hardness; dark greenish gray (5GY 4/1) to dark greenish gray (5G 4/1), dry, weak HCI reaction, very stiff consistency, weak cemen- tation, little mica, trace glauconite, gradual transition to adjacent lithologies (Marine).	ch
	~	75.0-76.0 m Fat clay with sand, (ch), 85% fines, high plasticity, slow dilatancy, medium toughness; 15% sand, fine, rounded, spherical, medium hardness; dark greenish gray (5GY 4/1) and dark greenish gray (5G 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, little glauconite, gradual transition with adjacent lithologies, sand content varies from 10-25% (Marine).	ch
	7	76.0-76.33 m Fat clay, (ch), 95% fines, high plasticity, no dilatancy, high toughness; 5% sand, fine, rounded, spherical, soft hardness; dark greenish grav (SGY 4/1) to dark greenish grav (SG 4/1), dry, weak HCI reaction, very	ch sc-
	7	stiff consistency, weak cementation, little mica, little glauconite, (Marine).	sm ch
		76.33-76.76 m Snity Cadyey Sand, SceSm), 60% Sand, line, rounded, spherical, medium hardness, 40% lines, medium plasticity, rapid dilatancy, low toughness; dark greenisk gray (SGY 41/1), moist, weak HCl reaction, weak cementation, little mica, some glauconite, gradual transition to adjacet lithologies (Marine).	sc- sm
		76.78-77.19 m Fat clay, (ch), 90% fines, high plasticity, no dilatancy, high toughness; 10% sand, fine, rounded, spherical, soft hardness; dark greenish gray (5GY 4/1) to dark greenish gray (5G 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, some glauconite, (Marine).	
		<ul> <li>77.19-77.87 m Silty clayey sand, (sc-sm), 60% sand, fine, rounded, spherical, medium hardness; 40% fines, medium plasticity, rapid dilatancy, low toughness; dark greenish gray (SGY 4/1), moist, weak HCI reaction, weak cementation, little mica, some glauconite, gradual transition to underlying lithology (Marine).</li> <li>77.87-80.6 m Fat clay, (ch), 95% fines, high plasticity, no dilatancy, high toughness; 5% sand, fine, rounded, spherical,</li> </ul>	ch
	7	soft hardness; dark greenish gray (5GY 4/1) to dark greenish gray (5G 4/1), dry, weak HCl reaction, very stiff consistency, weak cementation, little mica, trace glauconite, (Marine).	
	Ì	greenish gray (SGY 4/1) and dark greenish gray (SG 4/1), moist, strong HCI reaction, weak cementation, little glauconite, gradual transition to underlying lithology (Marine).	sc- sm
	Г	80.83-82.58 m Fat Clay, (ch), 95% tines, high plasticity, no dilatancy, high toughness; 5% sand, tine, rounded, spherical, soft hardness; dark greenish gray (5GY 4/1) to dark greenish gray (5G 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, trace glauconite, (Marine).	ch
	]	82:36-27.75 m Snty Catyey Sand, Sc-Smty, 70% Sand, line, rounded, spinetcal, me-dum naroness; 30% lines, medium plasticity, rapid dilatancy, low toughness; dark greenish gray (SGY 4/1) and dark greenish gray (SG 4/1), moist, strong HCI reaction, weak cemen- tation, little mica, little glauconite, gradual transition to underlying lithology (Marine).	sc- sm/
	ſ	82.75-83.25 m Fat clay with sand, (ch), 85% fines, high plasticity, no dilatancy, high toughness; 15% sand, fine, rounded, spherical, soft hardness; dark greenish gray (5GY 4/1) to dark greenish gray (5G 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation. Ittle mica, trace diauconite, gradual transition to adjacent	sc- sm
	1	lithologies (Marine). 83.25-83.83 m Sitty clayey sand, (sc-sm), 70% sand, fine, rounded, spherical, medium hardness; 30% fines, medium plasticity randi dilataory law touchness: dark preenish gray (SG 41) and dark greenish gray (SG 41) mist	ch
		strong HCI reaction, weak cementation, little mica, little glauconite, gradual transition to underlying lithology, some pockets of 100% sand (Marine). 83.83-84.5 m Fat clay with sand, (ch), 85% fines, high plasticity, no dilatancy, high toughness; 15% sand, fine, rounded, spherical, soft hardness; dark greenish gray (SGY 4/1) to dark greenish gray (SG 4/1), dry, weak HCI reaction, very stiff consistency, weak cementation, little mica, trace glauconite, gradual transition to adjacent lithologie. (Marine)	
	L	84.5-88.0 m Silty clayey sand, (sc-sm), 70% sand, fine to medium, subrounded, spherical; 30% fines, medium plasticity; grayish olive green (5GY 3/2), moist, weak HCI reaction, homogeneous, trace Glauconite grains, becoming sandier with depth, 80/20 to 90/10, sand with clay.	sc- sm
		88.0-97.43 m Poorly graded sand, (sp), 95% sand, fine to medium, subrounded, spherical; 5% fines; dark greenish gray (SGY 4/1) to grayish olive green (SGY 3/2), moist, weak HCI reaction, homogeneous, trace Glauconite grains, trace mica, fines content increasing with depth, to SP-SC.	sp

# OPERA

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