The role of the HADES URL in better understanding of the Boom Clay pore water geochemistry



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Abstract: When assessing a rock formation for its suitability as a potential host rock for the disposal of radioactive waste, knowledge about its pore water chemical composition is essential. When the HADES underground research laboratory became operational in the early 1980s, it offered the possibility of extracting pore water from Boom Clay. At the time, however, there was almost no experience of sampling pore water from deep clay formations. The low hydraulic conductivity of clays makes it difficult to extract pore water and the sampling process itself can induce changes in the observed chemical characteristics due to oxidation and re-equilibration with the ambient air. In the past decades, significant progress has been made in the techniques and protocols to sample and monitor pore water. The use of nitrogen instead of compressed air to drill boreholes and installing piezometers limited the disturbances induced by oxidation of the clay. Furthermore, an advanced system was developed to simultaneously sample pore water and dissolved gases and measure some key geochemical parameters such as pH, pCO₂ and redox potential under *in situ* conditions. This has resulted in a more reliable characterization of the Boom Clay pore water and a better understanding of perturbing processes such as oxidation.

In the framework of geological disposal of radioactive waste, it is important to characterize the pore water that is expected to come into contact with the deep geological repository. These characteristics are necessary to design the deep geological repository and evaluate the short- and long-term evolution of the geological disposal system as a whole. Characterizing and obtaining representative pore water have therefore received considerable attention in the different national research programmes during recent decades, in particular when considering clayey lithologies (e.g. NEA 2000; De Craen et al. 2004b; Tournassat et al. 2015; Wersin et al. 2022). However, extracting representative pore water samples can be challenging. The clay's low hydraulic conductivity and the important fraction of water bound as hydration shells to cations, which in their turn are strongly bound to the negatively charged clay minerals (NEA 2000; Yang et al. 2021; Fleury et al. 2022), can make it difficult to obtain sufficient water. In addition, when clay samples are exposed to atmospheric conditions, oxidation and re-equilibration with the ambient air occur which disturb the pore water composition.

The pore water composition of the clay host rock plays a role in a series of processes relevant to the safety assessment. The degradation of cementitious components, such as the backfill, is affected by the pH and chloride content of the water (Glasser et al. 2008). Assessing the corrosion of the steel components requires knowledge about the electrical potential and salinity (e.g. Kursten et al. 2011; Smart et al. 2014; Necib et al. 2017a, b). And once the disposal waste packages are breached and the radioactive waste comes into contact with infiltrating water, the dissolution of the radionuclides and their migration through the host rock must be assessed. This also requires knowledge about the composition of the pore water given its impact on the solubility and speciation of radionuclides assessed (e.g. NAGRA 2005; SKB 2005; Bildstein et al. 2007; Lemmens et al. 2012).

The pore water composition does not only affect the disposal system. The disposal system itself will also change the pore water composition. The Boom Clay was geologically deposited under anoxic conditions, making it susceptible to oxidation. Excavating the repository will create oxidizing conditions and can trigger microbial activity that might change the

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composition of the pore water. Other disturbances caused by the disposal system include the creation of an alkaline plume around cementitious backfill materials and a temperature increase where heatemitting waste is disposed. In the long term, natural processes, such as sea-level fluctuations, can also change the water composition. These possible induced and natural changes in the pore water chemistry need to be understood as well and their impact needs to be assessed.

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In the early 1980s the construction of the HADES underground research laboratory (URL) in Mol started. The URL is constructed 225 m below the surface in Boom Clay (Fig. 1). It played a crucial role in characterizing the pore water of the Boom Clay, as it allowed the extraction of pore water *in situ* from the Boom Clay. This also provided the opportunity to conduct experiments investigating how the pore water composition changes owing to perturbations such as oxidation around the URL or a thermal loading.

The HADES URL was the first laboratory worldwide to study pore waters from clay-rich formations, considered as potential host formations for radioactive waste repositories. As such, the HADES URL played a pioneering role and newer URLs such as Mont Terri in Switzerland or the Bure URL in France have taken advantage of the progress made in the HADES URL. In this context, the precise and coherent summary of pore water sampling and monitoring methods, together with their limitations, represents a valuable contribution, and helps to interpret pore water chemistry also in other clay formations (Delay *et al.* 2014; Tournassat *et al.* 2015; Bossart *et al.* 2017; Bleyen *et al.* 2019; Wersin *et al.* 2022). In this paper, we present the progress of the water sampling and measurement devices installed in the HADES URL. This progress was mainly due to experience gained from 40 years of sampling and analysing pore water. The paper explains how initially pore water was collected from filters mainly used to measure liquid pressures, but how over time filters were built with the specific purpose of collecting pore water. These filters were also installed at different depths to characterize the vertical variability of Boom Clay pore water.

The paper addresses the challenges to obtaining undisturbed samples. In particular, the Boom Clay's susceptibility to oxidation proved challenging. Several measures were taken to minimize this disturbance: glass bottles for collecting the water samples had water-gas seals and samples were treated in the laboratory under anaerobic conditions. However, the main breakthrough in minimizing oxidation came when it became possible to drill boreholes and install filters using nitrogen instead of compressed air.

The paper finally describes how an integrated *in situ* circulation system was developed. This allowed the measurement of a number of key geochemical parameters in real time and sampling of the pore water under *in situ* conditions. This also made it possible to monitor the impact of disturbances caused by the HADES URL or experiments performed in the URL.

These improvements led to an increasingly better understanding of the Boom Clay geochemistry at the Mol site. The most recent and complete understanding of the Boom Clay geochemistry at the Mol site was recently published by Honty *et al.* (2022*a*) and Wang *et al.* (2023).



Fig. 1. Layout of the HADES underground research laboratory, situated at a depth of 225 m in Boom Clay, Mol, Belgium. It can be reached through two access shafts. The main gallery linking these two shafts is *c*. 150 m in length.

The Boom Clay formation below the site of SCK CEN in Mol stretches from a depth between 185 and 287 m (Fig. 2). It was deposited during the Oligocene (Rupelian) in a marine environment, in the North Sea Basin (Vandenberghe *et al.* 2004). The grain-size distribution and organic matter content are remarkably cyclic (Vandenberghe and Van Echelpoel 1987; Vandenberghe *et al.* 2014), and also the carbonate content appears cyclic (Vandenberghe *et al.* 2022). It only underwent very limited diagenesis and compaction. The degree of overconsolidation is very limited, with a maximum literature value of 2.4 in Mol (Horseman *et al.* 1986).

As a clay to silty clay that underwent very limited diagenesis, the main compounds of the solid phase of the Boom Clay are detrital clay minerals and siliciclastic minerals, like quartz and feldspars. Both populations negatively correlate and together make up the major part of the solid phase. The rest fraction mainly consists of carbonate minerals (disperse occurrence and sometimes concentrated in the concretions) and organic matter (up to a few weight percent), of framboidal pyrite, with occurrences in the order of 1-5 wt% and of other accessory minerals or amorphous phases (Zeelmaekers et al. 2015; Frederickx et al. 2021). The clay minerals that are systematically present are smectite, illite, randomly interstratified illite-smectite, randomly interstratified kaolinite-smectite, kaolinite and chlorite (Zeelmaekers et al. 2015; Frederickx et al. 2021). Mainly the clay minerals, carbonate minerals, pyrite and organic matter are relevant for the aim of this paper, given their potential interaction with the Boom Clay pore water.

Pore water sampling techniques applied to Boom Clay

Already since the beginning of the research on Boom Clay as a potential host formation for the geological disposal of radioactive waste, a key question was how to obtain representative pore water from Boom Clay. Large amounts of pore water were needed for use in scientific experiments in the surface laboratories. Pore water samples were also needed to characterize the pore water chemistry and understand the underlying processes (adsorption, transport and interface reactions with different engineered barrier materials) involved in the geochemical and reactive transport modelling.

Boom Clay is a low-permeability argillaceous rock. Undisturbed Boom Clay has a hydraulic conductivity on the order of 10^{-12} m s⁻¹ (Yu *et al.* 2013). This makes it difficult to extract pore water. However, Boom Clay has a high water content (about 20 or 40 vol%). This means that virtually all standard pore water extraction techniques should in principle be technically feasible. Therefore, pore water extraction from Boom Clay was considered easy and relatively simple compared with, for example, the Swiss Opalinus Clay or the French Callovo-Oxfordian Claystone (NEA 2000 and references therein).

In the Belgian programme, pore water has been obtained in several ways, including both laboratory and *in situ* techniques. All of these techniques required the drilling of boreholes from the HADES URL either for the coring of clay samples as a source for pore water extraction in the laboratory, or to place



Fig. 2. Geological section in the Campine area, with indication of the HADES underground research laboratory at a depth of 225 m in Boom Clay under the Mol site. At this location, Boom Clay is *c*. 100 m thick and occurs at a depth of 185–287 m.

piezometers in the clay around the HADES URL for pore water sampling under *in situ* conditions. The drilling of boreholes in the HADES URL was done taking into account the specific conditions and limitations of an underground laboratory. Drilling, sampling and preservation of clay cores were done in such a way that all possible geochemical perturbations were minimized and according to the knowledge and best practice of that time.

Several techniques were used in the surface laboratories starting from an excavated clay core. The leaching method consists of crushing a clay sample and adding deionized water or another solution. Once a chemical equilibrium is reached, the liquid phase is analysed. Although this method is not straightforward in obtaining a reliable pore water composition (a leachate is added to the clay, leading to dilution of the originally present pore water and also stimulating different chemical reactions between the water and the rock), and the interpretation of the overall results often requires additional information about the clay mineralogy, mineral solubility, cation exchange capacity and fraction of anion accessible porosity (Bradbury and Baeyens 1998; De Craen et al. 2004b; Frederickx et al. 2018), this method is particularly interesting for measuring conservative anions such as chloride and bromide (Pearson et al. 2003).

This methodology was mainly applied to Boom Clay in the 1980s. The high porosity, plasticity and organic matter content of the Boom Clay result in a non-linear relationship between the solid/liquid ratio and the solute concentration of specific species, such as chloride or dissolved organic carbon. This complicates the derivation of the *in situ* water composition from the leachate and makes this method less applicable for Boom Clay.

Mechanical squeezing of clay cores serves as an alternative method for pore water sampling. Pore fluids are forced out of solid Boom Clay cores by mechanical pressure, similar to the natural process of consolidation but at a greatly accelerated rate. This technique is widely applied for low-permeability clays (Reeder *et al.* 1992, 1994, 1998; Reeder and Cave 1999; NEA 2000; De Craen *et al.* 2004*b*; Fernández *et al.* 2014). The advantage of this technique is that Boom Clay pore water can be studied from various boreholes drilled at different locations. With this perspective, Boom Clay samples from various boreholes in the Campine have been squeezed for geochemical studies (De Craen *et al.* 2000; De Craen 2001).

Squeezing experiments on Boom Clay cores indicated that the pore water chemistry remains more or less constant up to a pressure of 7.5–8 MPa, but significant chemical changes occurred at higher pressures (De Craen *et al.* 2000; similar observations in other studies are reported in NEA 2000; Fernández

et al. 2014). At an increased pressure, it is not clear whether only the free water or also part of the bound water is squeezed out of the clay. In addition, increased pressures reduce the pore size within the clay sample, which hinders large ions from being squeezed out of the clay core. Although the process is not yet fully understood, it is clear that the applied squeezing pressure influences the chemical composition of the extracted pore water. The limitations of this technique associated with the applied pressure could be avoided by defining a procedure in which all Boom Clay samples are squeezed at a relatively low and constant pressure of 7.5 MPa over a period of one week. This allows the collection of 40-50 ml of water from about 700 g of wet clay, and corresponds to about 30-35% of the total water content. Using this procedure, the squeezing technique is considered as a successful pore water extraction technique for Boom Clay. More information about this technique and its advantages and shortcomings can be found in De Craen et al. (2000).

Finally, pore water can be extracted *in situ* using piezometers. Piezometers are inserted into a borehole in the clay formation. They have one or more porous filter screens through which water can flow into a filter chamber (Fig. 3). By maintaining a lower water pressure in the filter than in the clay, pore water will flow into the filters. From there the water can flow through a capillary tube into a metal container or a glass bottle (filled with slightly overpressured argon) with a gas-water seal to prevent the sample from being perturbed by oxygen. This method has been applied in several URLs including HADES, Mont Terri (Switzerland) and Meuse/Haute Marne (Bure, France) (Pearson et al. 2003; Wang et al. 2004; De Craen et al. 2004b; Mazurek and de Haller 2017).

In order to place the piezometer in the borehole, the borehole diameter must be slightly larger than that of the piezometer. The resulting annular void is generally filled with a permeable material such as gravel. This is, however, not necessary for Boom Clay. Owing to its plastic behaviour, the clay will converge towards the piezometer and seal the annular void.

Since the HADES URL became operational in the 1980s, several piezometers have been installed in the HADES URL. Figure 4 gives an overview of the most important piezometers (with their past and current names) used to extract pore water samples.

An extensive evaluation of the three methods described above was published in 2004 (De Craen *et al.* 2004*b*). It was concluded that the most representative pore water composition for the *in situ* conditions of Boom Clay around the HADES URL in Mol was obtained from piezometers. This is because the pore water extracted by piezometers undergoes minimum laboratory manipulations, which reduces the disturbance of the samples. Moreover, in this

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Fig. 3. (a) A piezometer consists of a filter screen placed inside the clay through which water flows into a chamber; (b) filter chamber from which this water can be extracted with a capillary tube, either into a glass bottle or a metal container (c).

case only the free or unbound pore water is collected. Solutes and colloids (such as mobile organic material) will flow out simultaneously provided that they are small enough to pass through the hydrodynamic tortuous network of water conducting pores. An important lesson learned, however, is that perturbations to the clay and its pore water can be induced by the construction of the HADES URL and the installation and use of the piezometers (borehole drilling, piezometer installation and water extraction).

First pore water sampling using piezometers

The first filter elements installed in the HADES URL had a hydro-mechanical use, i.e. measuring the fluid pressure around the HADES URL. They were nevertheless used to collect large volumes of water for laboratory tests and for first geochemical analyses.

One of the first piezometers, installed in September 1983, was the S-1D piezometer (also known as EG/BS, 'Excavation Gallery/Bottom Shaft'; Fig. 5). It was directed vertically downwards below the First Shaft of the HADES URL (Neerdael 1984). Its primary goal was a 'reconnaissance drilling' to explore the geo-hydraulic characteristics of unfrozen Boom Clay below the HADES URL which was at that time constructed in frozen clay. A 32.5 m long metallic hollow supporting tube with a 0.6 m long stainless steel porous filter was placed in the vertical borehole below the shaft. The annular space between the piezometer and the clay



Fig. 4. Piezometers in the HADES URL that have been used for Boom Clay pore water studies (De Craen *et al.* 2019). (In the past, piezometers were often given an acronym or a name from Greek mythology. The older names are included in blue.)

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Fig. 5. Schematic drawing of the S-1D (EG/BS) piezometer-construction, shown at its location on the bottom of the First Access Shaft of the HADES URL. Depth below surface level. Source: from Neerdael (1984).

was filled with sand and gravel over a vertical section of 13 m. Because the sand/gravel yields a much higher hydraulic conductivity compared with that of the surrounding Boom Clay, the water flow towards the piezometer filter was governed by the dimensions of the sand/gravel column rather than by the dimensions of the porous stainless steel filter. Collecting water from such a long vertical interval has the advantage that it yields a relatively large amount of water. For many years, this piezometer was used to collect significant amounts of pore water for laboratory tests and for the geochemical characterization of Boom Clay pore water.

It is worth noting that the vertical interval of the gravel around this piezometer includes two layers of silt, called the 'Double Band'. Because these silt layers have a higher hydraulic conductivity (about factor 2–3), they yield more water than the surrounding clay layers. As a result, the water samples collected by this S-1D filter will be influenced by the composition of the water of the 'Double Band'. The samples may therefore not be representative of the pore water of the more clayey layers within the Boom Clay. However, at that time, this was not yet known because the pore water composition was considered to be homogeneous over the entire thickness of the Boom Clay layer.

The first attempts to characterize the chemical composition of Boom Clay pore water were made in surface laboratories. Aqueous leaching of clay cores and from the S-1D piezometer (Baeyens

et al. 1985; Henrion et al. 1985) gave the first data on the pore water composition of the Boom Clay. It was concluded that the Boom Clay pore water in Mol is equivalent to a 14.9 mmol NaHCO₃ solution, rich in humic acids with a large molecular size spectrum. These humic substances typically gave the pore water a dark colour, which also indicates the presence of colloids. Owing to the ionic diffusivities in compacted Boom Clay of around 10⁻¹⁰ m² s⁻¹ (Henrion et al. 1985), and the low hydraulic conductivity on the order of 10^{-12} m s⁻¹ (De Cannière *et al.* 1996), it was assumed that the pore water is in equilibrium with the solid phase and that the pore water composition is constant over the thickness of the formation. The chemical composition of these pore waters was therefore used for many years as the reference pore water composition of Boom Clay at in situ conditions at the Mol site.

Geochemical modelling on Boom Clay highlighted the need to determine key geochemical parameters such as the pH, pCO₂ and the redox potential $(E_{\rm H})$. Measuring these parameters in the surface laboratory often did not yield values representative of in situ conditions. It is well known that pore waters exposed to ambient air or pressure in the surface laboratory are prone to lose volatile gases, thereby affecting the pH system. The Boom Clay pore water contains dissolved CO₂ and is therefore sensitive to pH changes under atmospheric pressure. pH values ranging from 6.5 to 9.6 have been measured in surface laboratories. Such a wide range is considered unreliable for in situ conditions (Dierckx 1997; De Craen et al. 2004b). It was believed that this observed range was mainly caused by the loss of dissolved CO₂, but it could also have been influenced by other factors, such as the storage time of the sample, the storage temperature, stirring during measurement, the time the sample was in contact with air and on rare occasions by microbial activity if the water was left in contact with the atmosphere for extended periods of time.

Therefore, attempts were made to measure the pH directly in the HADES URL. However, the requirements for a representative *in situ* pH measurement are very demanding. The integrity of Boom Clay pore water has to be maintained during the *in situ* pH measurements. This requires measuring under *in situ* hydraulic pressure (2.25 MPa at the HADES level; Bernier *et al.* 2007) so as not to alter the pressure depending dissolution chemistry (e.g. calcite solubility and dissolved gases) avoiding contact of the Boom Clay pore water with the atmosphere to prevent gas exchanges (e.g. CO_2 loss or O_2 intrusion) and monitoring of the pH evolution to determine the moment of geochemical equilibrium and to quantify reaction kinetics.

Initially, classical laboratory devices were brought to the HADES URL to perform pH analyses



Fig. 6. Picture of the very first on the spot *in situ* measurement system for pH and redox potential ($E_{\rm H}$) to overcome the inevitable biases of classical laboratory measurements. The used pH and $E_{\rm H}$ analytical devices were capable of automatically storing 200 data points on a built-in memory.

there. This was done using flow-through cells with classical glass electrodes for pH measurement connected to piezometer filters (Fig. 6). This simple method initially gave more representative pH values (8.0–8.5). However, over time gas bubbles developed in the flow-through cells and tubing. This disturbed pH values, which could no longer be trusted. It became clear that *in situ* pH measurements were far from obvious and that further developments were needed.

Measuring the $E_{\rm H}$ also seemed impossible in a surface laboratory environment. Once isolated from its solid minerals, Boom Clay pore water has a very limited and almost non-existent redox buffering capacity. This is mainly caused by the redoxmorphic nature of iron species in anaerobic Boom Clay water that is in contact with the redox controlling iron minerals of solid Boom Clay host rock, pyrite and to a lesser extent siderite. Both minerals have very low solubilities. Therefore, they are unable to provide sufficient redox buffering capacity to the pore water once this water is isolated from the solid rock. As a result of this low mineral solubility, electrochemical measurements of the oxidation reduction potential of isolated Boom Clay pore water is quasi unfeasible. It is therefore almost impossible to determine the true $E_{\rm H}$ value of in situ Boom Clay water based on analytical oxidation reduction potential measurements of its isolated pore water. It thus became necessary to develop solutions to

measure $E_{\rm H}$ directly *in situ* under representative geological conditions.

The partial pressure of CO₂, pCO₂, is another essential parameter to model the geochemical evolution of Boom Clay. The measurement of pCO₂ is, however, far from obvious. Under normal Boom Clay *in situ* physico-chemical conditions (e.g. hydraulic pressure of 22.5 bar), no gas phases are present. All volatile and gaseous components are completely dissolved in the pore water. In undisturbed *in situ* conditions, CO₂ is the most dominant dissolved gas in pore water. Other dissolved gases may also be present but their concentrations are negligible.

Henrion was the first to try to measure the partial pressure of CO₂ in Boom Clay (Henrion *et al.* 1985). He assumed, in analogy with common CO₂ measurements on frozen pieces of pole ice, that a large piece of frozen Boom Clay would keep its initial content of CO₂. Frozen clay cores were collected when the First Shaft and First Gallery of the HADES URL were excavated in frozen clay (Li *et al.* 2022). The frozen clay cores were placed in aluminium-lined gas-tight bags. After unfreezing the clay cores, the CO₂ content in the gas-tight bags was measured. From this measurement the partial pressure of CO₂ was determined assuming the relationship with the dissolved carbonate system (CO₂, CO₂(aq), H₂CO₃(aq), HCO₃⁻, CO₃²⁻). This amounted to a value of 3.20 mbar (=10^{-2.5} atm) (Henrion *et al.* 1985).

At the end of the 1990s, the representativeness of the pore water composition derived from the S-1D piezometer was questioned. In 1997, Dierckx published a report on 'Boom Clay *in situ* pore water chemistry' (Dierckx 1997). In this report, a mean value for the ionic composition of the S-1D piezometer was presented and compared with other piezometers. It was concluded that the S-1D piezometer was not an optimal piezometer to study Boom Clay pore water and that more measurements were needed to better understand the Boom Clay pore water chemistry.

This led to the installation of the TD-116 piezometer: a 13 m long horizontal piezometer with four porous filters, each 1.52 m long. This piezometer is used to sample large amounts of Boom Clay pore water at the middle level of HADES URL, for use in laboratory tests.

Vertical piezometers to characterize the vertical variability of Boom Clay pore water

During the 1980s and 1990s the Boom Clay pore water was considered homogeneous over its entire stratigraphic thickness. Boom Clay is characterized by a banded structure. A banded structure does not

necessarily imply variations in pore water composition, but as in Boom Clay the banded structure is the result of variations in grain size (also reflected in the (clay)mineral contents), organic matter content and carbonate content (Vandenberghe *et al.* 2014), and these might influence the pore water composition, the question was raised if the variability was also reflected in the pore water composition. Moreover, it was known that different pore water samples yielded a different coloration, possibly pointing to a link with the organic matter.

Therefore, the vertical piezometer TD-11D and MORPHEUS ('Mobile ORganic matter and Pore water extraction in the HADES Experimental Underground Site') experimental setup was installed in 2001 in the Test Drift of the HADES URL. It was the first piezometer specifically designed to study the variability of the Boom Clay pore water composition (including the dissolved organic matter content) at different stratigraphic levels (Maes et al. 2004; De Craen et al. 2004a). This piezometer allowed pore water sampling from 12 distinct horizontal stratigraphic layers varying in lithology, total organic matter and carbonate content. The variations in the pore water composition as observed in the TD-11D piezometer furthermore served to calibrate the geochemical model and to generate a new reference pore water composition at the Mol site (De Craen *et al.* 2004*b*).

A first takeaway from this new piezometer was that the initial high dissolved organic carbon (DOC) concentrations measured during the initial stage of the pore water sampling (up to about $350 \text{ mg } \text{Cl}^{-1}$ decreased with time and finally reached a stable concentration (average 115 mg C 1^{-1}) after about 3 years. The initially high DOC contents were attributed to the effect of oxidation during drilling and piezometer installation. This caused part of the immobile organic matter fraction to become mobile (Van Geet 2004). It was also found that DOC concentrations are not correlated to the solid organic matter content in the studied layers. This is not surprising given the later studies (Durce et al. 2015) which showed that mobile organic matter accounts only for about 0.15% of the total organic matter inventory in the Boom Clay. The highest DOC concentrations (about 200–250 mg $C l^{-1}$) were observed in the 'Double Band'.

This is in line with the current understanding of the dissolved organic matter behaviour in the Boom Clay and relates to clay transport properties such as filtration and sorption. The controlling mechanisms behind the DOC concentrations in Boom Clay are rather complex. The most influential parameters are pore size distribution, pore connectivity, pore throat diameter, size distribution of the dissolved organic matter and mineralogy, notably the ratio between clay and silt (Durce *et al.* 2015). The dissolved organic matter in Boom Clay has a bimodal molecular weight distribution. The relative abundance of large v. low molecular weight entities is mostly controlled by the relative silt/clay content. The clay minerals preferentially filter large organic molecules (molecular weight (MW) >20 kDa, hydrodynamic radius (Rh) >2.8 nm), while favouring the transport of the small entities (MW <20 kDa, Rh <0.3–2.8 nm). On the contrary, coarser grains favour the transport of dissolved organic matter containing high MW organic species (MW >20 kDa) owing to limited sorption and relatively higher porosity. These findings explain well the variations of the dissolved organic matter as observed in the pore waters of the TD-11D piezometer.

Another observation is related to the homogeneity of the Boom Clay pore water composition at the Mol site. Overall, the Boom Clay pore water composition at the Mol site is a NaHCO₃-type water, showing a flat depth-profile over the entire stratigraphic depth, with only very limited variations in Na⁺, HCO₃⁻, Cl⁻, Ca²⁺ and DOC.

In 2001, several new reconnaissance boreholes were drilled in the newly excavated Connecting Gallery (at different locations and in different orientations around the HADES URL). These were equipped with multiplezometers whose initial purpose was to monitor the pressure evolution within the clay massif. However, the piezometers can also be used to study variations in the pore water chemistry. The CG-13U and CG-13D piezometers (Fig. 7), installed in 2003, provided the opportunity to further explore the vertical spatial variability of the Boom Clay pore water composition at the Mol site (up to 20 m above and 40 m below the gallery, respectively; De Craen 2005). This resulted in an extended dataset, including the pore waters from these two piezometers, so that the compositional range of values could be derived for the Boom Clay pore water at the Mol site over a 65 m thick interval (Table 1, Honty et al. 2022a). The mean chemical composition of Boom Clay pore water is defined here as the average composition of the 195 pore waters as presented in the work of Honty et al. (2022a). The motivation to derive such mean pore water composition is discussed later in the paper in the section 'Improved understanding of the Boom Clay geochemistry'.

This dataset further confirms the overall homogeneous composition of Boom Clay pore water at the Mol site, being a NaHCO₃-type water over the entire depth, with only limited compositional variations. More detailed observations show, however, a nearly linear vertical trend, mainly expressed in the Na⁺, HCO₃⁻ and Cl⁻ concentrations (see Honty *et al.* 2022*a*, fig. 8). These are explained by a simple outdiffusion starting at the time when the area of Mol emerged from the sea (Mazurek *et al.* 2009). Given



Fig. 7. (a) The CG-13D piezometer underneath the HADES URL and (b) the CG-13U piezometer above the HADES URL represented with the Boom Clay lithology. Dark layers represent clayey layers; light layers with dots represent silt-rich clay layers; ovals represent carbonate concretions. Piezometer filters are indicated as R13D-xx. Depth (red numbers) is in metres intrados. Source: De Craen (2005).

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 Table 1. The Boom Clay compositional ranges observed at the Mol site

Composition	Range mg 1 ⁻¹	Mean mg l ⁻¹	Standard deviation mg 1 ⁻¹	
				Na
K	5.3-12.1	8.2	1.67	
Ca	1.15-3.9	2.4	0.99	
Mg	0.94-2.67	1.7	0.58	
Sr	0.029-0.097	0.06	0.02	
Fe	< 0.02-0.71	0.31	0.42	
Si	3.05-8.5	5.3	2.39	
Al	< 0.02-0.12	0,05	0,04	
TIC (mg C l^{-1})	92.2-225	147	38	
alkalinity (meq 1^{-1})	8.5-18.3	12.8	2.34	
Cl	12.3-32	20.1	4.5	
SO_4^{2-}	< 0.25-4.66	1.45	1.76	
F	1.43-3.54	2.38	0.65	
Br	< 0.25-1.09	0.52	0.3	
I	0.42-0.91	0.62	0.11	
В	4.3-9.4	6.62	1.98	
DOC (mg C l^{-1})	24-180	88	67	
pH in situ	7.7-8.7	8.2	0.2	
pH laboratory	8–9	8.5	0.4	
log pCO ₂ (atm)	-2.88 to -2.38	-2.58	-3.07	
$E_{\rm H} ({\rm mV})$	-328 to -310*	-317	7	
$E_{\rm H} ({\rm mV})$	-224 to -234**	-230	6	
Temperature (°C)	16	-	-	
EC (μ S cm ⁻¹)	830-1768	1540	1350	
Ionic strength	0.01-0.02	0.013	-	

Calculated redox potential $(E_{\rm H})$ values based on the *sulfate-thiosulfate redox pair and the *siderite-pyrite redox pair. For details of the calculation and used thermodynamic database, the reader is referred to Honty *et al.* (2022*a*). EC, electrolytic conductivity.

the constant qualitative mineralogical composition of the Boom Clay at the formation scale, the small local variations in the pore water composition are rather linked to the variable silt/clay ratios in the specific layers.

Note that lateral compositional variations have been observed at a regional scale, with more saline compositions towards the northwestern part of Belgium, e.g. Essen, and also with a vertical almost linear trend of increasing Cl^- and Br^- concentrations (De Craen *et al.* 2006). The setting is very similar to that of Mol, with the exception that emergence from the sea occurred more recent in time, resulting in the observed trend (Mazurek *et al.* 2009).

Measuring key geochemical parameters (pH, E_H, pCO_2) at *in situ* conditions

Over the years a lot of progress has been made to measure these parameters in real time and under *in situ* conditions. The stepwise improvements in measuring these key geochemical parameters are discussed below.

1992 - the ARCHICHIMEDE-Argile project:detailed study of the Boom Clay pore water chemistry and further attempts to measure pH and E_H in situ

In 1992, a study was started to better characterize the pore water chemistry of Boom Clay (Griffault *et al.* 1996). Therefore, two horizontal multifilter piezometers, A-6E and A-24E, were installed with the specific purpose to obtain samples for pore water analysis and to perform *in situ* physicochemical measurements. The boreholes were drilled using compressed air to remove the clay cuttings. No gravel or sand was used to backfill the space between the piezometers and the clay. Instead, the clay was allowed to gradually seal around the piezometer. Owing to the high *in situ* stresses (4.0 to 4.5 MPa) and the plasticity of the clay, this happened in a relatively short time (in the order of a few weeks).

The A-24E piezometer is a 16.2 m long horizontal piezometer with five 60 mm long filters. Its sole purpose was to collect chemically undisturbed Boom Clay pore water in geochemical equilibrium with the dissolved carbon dioxide gas concentration, typically expressed as partial pressure, pCO₂. To realize this, small-sized filters were used, each with only one single water line with small, almost capillary sized, internal diameters. This was done to reduce as much as possible the dead volume or static water amount inside the piezometer(s). Sampling was performed with special pinched close copper sampling tube(s), with low internal volumes of a few 10^{-6} m³ (=a few cm³) that were directly connected onto the piezometer waterline(s). These copper sampling tube/vial (s) remained connected to the waterline for several months, in an attempt to obtain borehole water that was in equilibrium with the dissolved gases. Unfortunately, chemical and microbiological analyses of these pore waters showed that artefacts could not be avoided, owing to both oxidation and microbial processes.

The A-6E piezometer is a 16.2 m long horizontal piezometer (with a diameter of 140 mm) with five 200 mm long filters. First, a series of welllocated Boom Clay cores were drilled with a hollow core taker, out of borehole A-6E, for solid and microbiological analyses. Measures were taken to avoid external chemical and microbiological contamination, but unfortunately, the nonsterilized compressed air used during the drilling operation disturbed the borehole geochemistry and microbiology. Secondly, the multipiezometer was installed. Its filters were specifically located on the same positions as the previously taken clay cores. Moreover, the deepest filter was equipped with one waterline having an internal diameter of 6 mm and placed at the bottom of the filter chamber. This was also specifically adapted to allow installing an optical pH fibre sensor in the filter chamber. Such an optical fibre sensor is based on colorimetric principles. The measurements revealed an in situ pH value of 8.2. The simplicity of the colorimetric principle is its main advantage, but colorimetric techniques suffer from a lack of accuracy: ± 0.1 pH units on the measurement is the best accuracy that can be achieved (Jobmann et al. 2005). A second important drawback of colorimetric methods is that they are often difficult to interpret, especially for coloured samples (e.g. colour changes in coloured samples, as in Boom Clay pore water). Therefore, colorimetric methods can only give a rough indication of the pH value (Jobmann et al. 2005; Higgins 2014). Furthermore, the period for which the stagnant pore water was monitored inside the filters of the piezometer was only two weeks. This is most likely much too short for the pore water to regain chemical equilibrium with its re-dissolving natural gases.

For completeness, it is worth mentioning that the ARCHIMEDE–Argile project encountered some unsuccessful tests as well, such as the *in situ* monitoring of the dialysis experimental drift, the *in situ* measurement of the cationic exchange Capacity by spectroscopic monitoring of hexamminecobalt(III)chloride, the *in situ* measurements of pH and E_H using microelectrode probes, and the evolution of the stable isotopes concentrations of clay water during a freezing cycle using an *in situ* microfreezing experimental setup. This has driven us to further continue investigations for new developments.

2000 - the ORPHEUS experimental setup: in situ measurement of pH and E_H in a closed circulation system

A major breakthrough was achieved by the ORPHEUS setup ('Oxidation Reduction Potential and pH Experimental Underground Station') developed in 2000 (Fig. 8) (Moors *et al.* 2002). The setup was composed of a flow-through cell equipped with robust and rugged solid-polymer filled pH and $E_{\rm H}$ electrodes (Xerolyt[®], Mettler-Toledo). These were the best pH and $E_{\rm H}$ glass electrodes available at that time. They were able to withstand high hydraulic pressure (>10 bar) and give reliable values over a long period of time (several years).

Four different types of oxido-reduction potential electrodes (i.e. platinum, gold, glassy carbon and an in house made pyrite electrode) were used to determine in a reproducible way a reliable $E_{\rm H}$ value for Boom Clay pore water. The flow-through cell was mounted between the inlet and outlet of a piezometer filter as part of a closed water circulation circuit. Water circulation was a mean to obtain, in a very fast way, an excellent chemical contact of the circulating pore water with the solid phase of the clay. As the system was closed, chemical equilibrium between re-dissolved natural gases, the circulating pore water and the surrounding solid clay could be reached in a short period of time.

The Xerolyt[®] electrodes were sufficiently robust to ensure long-term stability while providing the accuracy and reliability of analytical glass electrodes. A circulation pump (pumping rate 10–20 ml per minute), free of any metal parts, guaranteed chemically undisturbed water circulation inside the closed circuit. A data acquisition system monitored



Fig. 8. (a) Schematic presentation of the ORPHEUS setup connected to the TD-116W piezometer, and (b) the ORPHEUS experimental setup as built.

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the evolution of the pH and $E_{\rm H}$ signals to indicate when geochemical pH equilibrium and a stable geochemical redox environment were reached. A controlled-atmosphere cabinet (argon flushed) hosted the entire flow through cell and the pump of the complete $pH-E_H$ measurement system. This controlled-atmosphere cabinet provided extra protection of the experimental setup against unwanted chemical interactions of reactive atmospheric gases like oxygen. At the end of a measurement campaign, which typically lasted a few months, the measurements were corrected for electrode drift (see Annex 3 in De Craen et al. 2004b). A drift of the reference potential of the built-in reference electrode system (type Ag/AgCl in 3 M KCl) was noticed, owing to KCl leaching of the reference electrode into the pore water (owing to the lower KCl concentration of the circulating pore water). The raw measurements were corrected by measuring the potential difference between the used reference electrodes and a new reference electrode (ref-ref measurements) and considering a linear drift evolution over time.

With this closed circuit, a representative *in situ* pH of 8.5 ± 0.5 could be measured, minimizing oxidizing perturbation and without the possible interferences of dissolved metal ions. With regard to the $E_{\rm H}$ measurements, it is noteworthy to mention that platinum and gold electrodes rendered very similar $E_{\rm H}$ values of -275 ± 25 mV (Moors *et al.* 2002), while glassy carbon was not sensitive enough and only gave erratic results. The prototype pyrite redox electrode resulted in a potential of 0 mV, suggesting that the redox condition of the Boom Clay is indeed controlled by pyrite (siderite) minerals.

An important lesson learned was that, despite this sophisticated measuring system, and all the precautions taken to reliably measure the in situ pH of the Boom Clay pore water, long-term pH measurements can cause perturbations of the system. The ORPHEUS setup showed that KCl leaching from the Xerolyt[®] reference electrodes could not be avoided (De Craen et al. 2004b). Owing to the continuous circulation of the pore water between the measuring flow through cells containing the Xerolyt[®] filled electrodes and the filter of the piezometer, KCl leaked into the pore water. The circulating pore water accumulated high concentrations of K⁺ and Cl⁻ ions. Elevated K⁺ concentrations induced cation exchange reactions, as was evidenced by the associated elevated concentration of Na⁺, Ca²⁺ and Mg²⁺ ions in the pore water. It was supposed that K⁺ ion exchange with Ca²⁺ ions on clay surfaces is accompanied by calcite precipitation and proton release. However, it is not known to what extent such a reaction lowered the measured pH. Another problem is the fact that Xerolyt electrodes also leached organic substances that were most likely a source of nutrients

for bacteria. The impact of this microbiological contamination on the pH and $E_{\rm H}$ measurements could, however, not be quantified. It was clear that it remained a challenge to further improve the experimental setup to obtain more representative measurements. Note that similar observations were made in the pore water chemisry experiment at the Mont Terri Rock Laboratory (De Cannière *et al.* 2011).

2004 – the PEGASUS experimental setup: circulation system especially designed for the sampling of dissolved gases and the measurement of pH under in situ conditions

In addition to a more accurate pH, the accurate determination of representative in situ pCO2 values for Boom Clay pore water became a priority. This was driven by an increased understanding of the significance of the dissolved carbonate system (e.g. pH controlling mechanism, pH buffering towards perturbing conditions) for radionuclide migration and speciation (De Craen et al. 2004b). Therefore, an innovative setup was designed in which the experimental boundaries are imposed and controlled by the Boom Clay formation itself. This design led to the PEGASUS ('Partial Pressure Evolution of Dissolved Gases in Real Underground Situations') experimental setup connected to the A-24E piezometer (Fig. 9) (Moors et al. 2005; Kele et al. 2006).

The main idea behind this novel pCO_2 measurement approach was to bring undisturbed *in situ* Boom Clay pore water in contact with an artificial, chemically non-reactive, inert gas like argon (Ar) under the same naturally occurring hydraulic pressure. As a result of this liquid–gas contact, the dissolved carbon dioxide starts to transfer from the liquid phase into the gaseous phase until the carbon dioxide concentrations of the two phases are in equilibrium. At chemical equilibrium the distribution of the carbon dioxide between the gas and the liquid phase is defined by the Henry's law. This states that the concentration of a gas dissolved in a liquid is proportional to the partial pressure in the gas phase.

Periodically, CO_2 concentrations are measured in the Ar gas phase and after a certain time (typically several months, depending on the influx rate of pore water/dissolved CO_2 in the vessel and the amount of pore water/dissolved CO_2 in the clay) the equilibrium will be reached as indicated by stable CO_2 values.

It was shown that the PEGASUS setup works and is a suitable technique to accurately measure *in situ* partial gas pressures. The principle of linear proportionality stated by Henry's law is reliable and can be applied to determine the concentrations of dissolved



Fig. 9. (a) Schematic representation of the PEGASUS experimental setup for the sampling of dissolved gases, and (b) a picture of the experimental setup as built.

gases in host rocks. The best value of the carbon dioxide partial pressure measured *in situ* with the PEGASUS setup is 2.85 mbar (= $10^{-2.55}$ atm).

2004 – the NF-PRO experimental setups: improved and integrated methodology for borehole drilling and piezometer installation, an experimental setup for the simultaneous sampling of pore water and dissolved gases, and measurement of key geochemical parameters at in situ conditions

As already mentioned, Boom Clay was deposited under anoxic conditions, making it susceptible to oxidation. The oxidation of pyrite and organic matter, both omnipresent in Boom Clay, affects the composition of the pore water (De Craen et al. 2008; Blanchart et al. 2012). Oxidation of pyrite results in the release of Fe^{2+} , SO_4^{2-} and acidity (protons) into the pore water, while organic matter oxidation generates dissolved organic matter. Therefore, measures are needed to avoid or at least minimize the oxidation of the clay. Piezometer filters were sealed from the atmospheric conditions in the HADES URL, glass bottles for collecting the water samples had water-gas seals and samples were treated in the laboratory under anaerobic conditions. However, oxidation could never be completely avoided because the borehole itself was drilled with compressed air. The use of inert gases, such as nitrogen or argon, instead of air was not allowed for safety reasons.

However, this changed after the Second Shaft was built and a new forced ventilation system was installed in 2002. This made it possible to drill using nitrogen instead of compressed air. This entered a new episode for the geochemical research in the HADES URL.

The first drillings performed with nitrogen gas (TD-41E and CG-64) were done in 2004 in the frame of the EC NF-PRO project (Near Field Processes, De Craen et al. 2008, 2011). To protect the borehole from oxygen when withdrawing the drill rods and inserting the piezometer, nitrogen was injected through two small holes drilled in the concrete lining around the borehole (Fig. 10). All piezometer filters and tubes were also flushed with nitrogen to remove all oxygen. After the piezometer was installed, a flange with a rubber joint was screwed over the entrance to the borehole and a limited but continuous flow of nitrogen was maintained through the small holes in the lining until it was clear that clay convergence had sealed the gap in the clay around the piezometer. At the end of the piezometer installation, polyurethane foam was injected behind the gallery lining to fill any remaining gaps.

Apart from drilling the TD-41E and CG-64E piezometers using nitrogen, an *in situ* circulation system was designed for these piezometers. The purpose of the system is to sample pore water and dissolved gases under *in situ* conditions, and for *in situ* pH measurement. Such a circulation system was created in-house. A schematic overview of this circulation system is given in Figure 11.

The circulation system can only be connected to one filter at the time. The two tubes coming from the filter chamber inside the piezometer are connected to the circulation system. The Boom Clay water initially penetrates the experimental system, until the hydraulic pressure is equalized, meaning that from that moment on, the water pressure in the experimental setup is the same as the one in the



Fig. 10. (a) Borehole drilling: two small inclined boreholes are drilled for continuous flushing with nitrogen to prevent oxygen perturbation during drilling of the borehole and emplacement of the piezometer. (b) Installation of the piezometer (from left to right): the piezometer is pushed into the Boom Clay, sealing off of the piezometer to avoid oxygen penetration from the gallery into the piezometer and screwing a rubber seal between the concrete lining and a flange. Source: De Craen *et al.* (2011).

Boom Clay environment. A pump circulates the pore water, in a closed circuit, through the experimental setup. To minimize the disturbance of the *in situ* hydrostatic equilibrium pressure in the vicinity of the filter screen, the rate of pumping is set and controlled to generate only a limited hydrodynamic pressure increase owing to the forced advection (= typical of a limited increase of 0.5 bar). By



Fig. 11. (a) Schematic layout of the *in situ* circulation system for the pore water sampling, sampling of the dissolved gases and measurement of the pH, and (b) a picture of the experimental setup as built. Source: De Craen *et al.* (2008, 2011).

circulating the water around in the closed system, the water composition at every location inside the experimental setup will match the composition of the interstitial pore water in the vicinity of the filter screen. In general, a few weeks to months are needed before geochemical equilibrium is established between the Boom Clay pore water and the water present in the experimental setup.

Three separated modules were connected to the circulation system. By opening the valves, the Boom Clay pore water is allowed to circulate through these modules. A first module is to sample the *in situ* Boom Clay pore water. A second module is to measure some important *in situ* geochemical parameters such as pH, temperature, $E_{\rm H}$ or the electrolytic conductivity. The third module is to characterize and measure dissolved gases within the Boom Clay pore water, based on the methodology used in the PEGASUS experimental setup (see earlier).

Sampling in these sophisticated circulation systems is done with the aid of metallic sample containers. Also dissolved gases can be sampled with the same type of metallic containers with the simple quick connector system. However, gas sampling requires a specific design and mounting of the metallic sample container inside the circulation circuit. Under 'standard' conditions the metallic sample container or multiple containers are integrated in the water circulation system.

These improvements – nitrogen drilling and the use of an *in situ* circulation system – allowed sampling of the pore water under *in situ* conditions and thus in real time. As a result of the new methodology, minimizing possible disturbances as much as possible, the obtained pore waters were more representative of *in situ* conditions compared with the waters sampled before. The improvements led to a better characterization of the Boom Clay pore water composition and hence a better understanding of the geochemical processes controlling the Boom Clay pore water geochemistry in undisturbed conditions. One remaining limitation in the NF-PRO setups was related to the leakage of KCl of the pH electrodes.

The improvements also opened up the possibility of monitoring the impact of disturbances caused by the HADES URL, such as the impact of the oxidation zone around the HADES galleries. In fact, the NF-PRO experimental setups were especially designed to study oxidation phenomena in Boom Clay as a result of the excavation of the main HADES gallery. The use of N₂ enabled the study of oxidation phenomena around the HADES URL, without additional oxidation owing to borehole drilling. This allowed the 'oxidation front' to be seen, e.g. the zone around the HADES galleries disturbed by oxidation. Oxidation was mainly expressed by high sulfate concentrations (sulfate is absent in

undisturbed Boom Clay pore water at the Mol site), the result of the oxidation of pyrite which is omnipresent in Boom Clay. The high sulfate concentrations were associated with higher concentrations of most cations, which is explained by mineral precipitation/dissolution reactions and cation exchange (De Craen et al. 2008, 2011). Oxidation phenomena were observed close to the gallery, decreasing rapidly further away from the gallery, until undisturbed conditions were reached at about 1 m away from the gallery lining. The same observations were made in the Test Drift (a 20 year-old gallery at that time) and the Connecting Gallery (2 years old at that time). Based on the obtained results, a conceptual model could be developed explaining oxidation around galleries in Boom Clay (De Craen et al. 2008, 2011).

2006 – the PRACLAY and experimental setups: integrated methodology as described above, slightly adapted

In preparation of the large-scale PRACLAY Heater Test, new questions arose regarding the effect of oxidation (as a result of the excavation of the PRA-CLAY Gallery – 2007), and regarding the effect of increased temperatures (owing to the PRACLAY Heater Test – since November 2014) on the pore water composition.

The PRACLAY Heater Test, simulating the thermal disturbance induced by the disposal of heat emitting waste, was launched in 2014. For at least 10 years, a 30 m long section of the PRACLAY Gallery has been heated to a temperature of 80°C at the interface between the gallery lining and the clay (Dizier *et al.* 2016, 2021). The main goal of the test is to characterize the thermo-hydro-mechanical behaviour of Boom Clay at large scale. The PRA-CLAY Heater Test, however, also offers the opportunity to monitor the impact of that temperature increase on the geochemistry of the Boom Clay.

In 2006, two piezometers, CG-30E and CG-35E, were installed next to the future PRACLAY Gallery. In each piezometer, three selected filters are connected to a separate circulation system. The design of the circulation system, although slightly adapted, is similar to that described above (Fig. 12). For the sampling and analyses of the filters closest to the PRACLAY Gallery, special requirements were needed for the follow-up of the pore water chemistry upon heating, resulting in a more complex design. For these filters, insulated water tubes and a heating system are foreseen which will keep the temperature inside the barrel the same as that of the water in the filter, in order to try to keep the water in the whole circulation system at a constant temperature for



Fig. 12. In situ circulation system for the pore water sampling, sampling of the dissolved gases and measurement of the pH in the frame of the PRACLAY Heater Test.

correct measurement of the governing geochemistry during the heater test.

In the meantime, the experimental setup has been further improved. At the end of 2007, a first improvement was needed as the water was not well pumped around. To solve this problem, the location of the pump in the circulation system was moved, so that the pump was located behind the barrel. Another change in the design is related to the *in* situ pH measurements. As KCl leaching occurred from the pH electrodes, the pore water in the circulation systems became enriched in K and Cl. In order to avoid this perturbation, the design of the experimental setup was adapted so that the pore water which circulated over the pH electrode in the by-pass loop during pH measurements could be removed from the circulation system via the outlet valve. However, for a few years, the classical KCl leak prone electrodes have been no longer in use. They have been replaced by the leak-proof REFEXTM electrodes (RefexSensors, Ireland). These electrodes can withstand high hydraulic pressures and their good long-term performance under in situ conditions has been demonstrated by Bleyen et al. (2019).

Improved understanding of the Boom Clay geochemistry

The knowledge of the Boom Clay pore water composition and underlying controlling processes is of importance for the understanding of the future evolution of the disposal system hosting the radioactive waste. Owing to interaction of the pristine Boom Clay with the engineered materials, the Boom

Clay pore water composition will progressively change, thereby possibly affecting the fate of the radionuclides in the repository near field. A first synthesis of pore water geochemical data was performed in 2004 (De Craen et al. 2004b). De Craen et al. also formulated a reference composition: the Boom Clay pore water at the Mol site was found to be a 15 mmol NaHCO₃ solution containing a significant amount of dissolved organic matter (about $115 \pm 15 \text{ mg C}$ l^{-1}). This reference composition was partly based on a geochemical model which was calibrated against experimental data from the TD-11D piezometer. Significant uncertainties remained because the model was based on a relatively small dataset and important parameters, such as pH, $E_{\rm H}$ and pCO₂, could not be measured directly and had to be derived by modelling at that time. The work published in 2004 identified the need for clear sampling and analyses procedures (De Craen et al. 2004b), and the accurate measurement of in situ geochemical parameters.

The year 2004 can be considered as an important milestone, as drilling with nitrogen became possible. Also, in the same period, the introduction of an advanced circulation system for the simultaneous pore water and gas sampling and the measurement of pH and $E_{\rm H}$ was a big step forward. These technological improvements were accompanied by organizational improvements, for example with the introduction of standardized sampling and analysis protocols, and the introduction of a centralized database GSIS, designed to manage the HADES infrastructure (boreholes, piezometers and filters), samples and geochemical data.

Table 2 summarizes the main improvements. Since these were mainly implemented around

Classical methodology	Improved and integrated methodology
Drilling using compressed air	Drilling using nitrogen (including nitrogen flushing during piezometer installation)
Open flow system	Closed circulation system
Sampling and parameter analysis was not done systematically	Sampling was done on a systematic basis and all-in analyses were performed on the samples, resulting in a large database
The reference pore water composition is based on 44 pore waters obtained from a limited part of the Boom Clay	The reference pore water composition is based on a more robust dataset of 195 pore waters spread over a depth interval of 65 m
No isotopic analyses of the gas phase or microbial research	Isotopic analysis of the gas phase and microbial analysis including DNA sequencing
No operating procedures or data management system in place	Use of operating procedures and data is incorporated in a geo-scientific information system

Table 2. Main improvements in pore water sampling and monitoring in the HADES URL

2004, that year was, somewhat arbitrarily, chosen to make a before/after comparison.

In the meantime, more reliable and representative data have been obtained, resulting in a high-quality dataset including representative measured values for the $E_{\rm H}$, pH and pCO₂. These form the base for a better understanding of the Boom Clay geochemistry.

The in-house extension of the analytical capabilities including gas mass spectrometry significantly reduced the time between sampling and actual analysis of the gas phase. Presently, simultaneous pore water and gas sampling have become a routine practice in the nitrogen installed piezometers. In addition to gas composition, the isotopic analysis of ¹³C and 18 O of the CO₂ gas emerged in the more advanced phase. The isotopic studies of the CO₂ gas suggested a strong link between organic matter degradation and CO₂ isotopic signature on the one hand and its isotopic equilibrium with the secondary carbonate minerals on the other (Gaucher et al. 2010). These findings are in line with the current understanding of the CO₂ origin and geochemical behaviour in the Boom Clay environment (Honty et al. 2022a).

Microbial activity in pristine Boom Clay at the Mol site is absent (for example owing to the very small average pore size of 15 nm, while the smallest living microbes have a diameter of 100 nm). However, the presence of microbes and microbial activity near the vicinity of the HADES gallery suggests human-induced perturbations of the host rock (owing to excavation of galleries, borehole drilling, etc., leading to local porosity changes) and possible contamination during installation of experiments. Similar observations have been made near the Mont Terri rock laboratory in Switzerland (Leupin et al. 2017). In the past, the fast convergence of Boom Clay around newly installed piezometers, and not using the first amounts of water collected, was assumed to be sufficient to avoid bacterial

disturbances in the pore water samples and analyses. In 2011, the presence and activity of the bacterial communities in Boom Clay pore waters collected from piezometer filters were evidenced for the first time by SEM and ATP measurements. Next, DNA extraction, polymerase chain reaction and next generation DNA sequencing allowed for the classification of specific bacterial (sub)phyla on selected samples of the TD-11D piezometer (Wouters et al. 2013). More recently, the presence of various Archaea (including methanogens) was confirmed in the piezometers CG-30E and CG-35E based on DGGE (denaturating gradient gel electrophoresis) and polymerase chain reaction amplicon sequencing (Mijnendonckx et al. 2019). It is generally accepted that the presence of an active microbial community, whether indigenous reactivated or externally introduced by human activity, may have a substantial impact on the measured Boom Clay pore water composition. Therefore, microbial analyses are currently performed systematically in combination with Boom Clay pore water chemistry and gas analyses.

The main conclusion is that the Boom Clay at the Mol site has an overall homogeneous pore water composition that can be approximated by a 13 mmol NaHCO₃⁻ solution with a significant amount of dissolved organic carbon (88.1 + 67 mg) 1^{-1}). Its average pH is 8.2 \pm 0.2 based on the *in situ* measurements and 8.5 \pm 0.4 based on the laboratory measurements. The pCO_2 values range between 1.34 mbar (= $10^{-2.88}$ atm) and 4.22 mbar (= $10^{-2.38}$ atm) with an average value of 2.67 mbar $(=10^{-2.58}$ atm). These values are considered to be the most complete and up-to-date reference of the pCO₂ in the Boom Clay pore water at the Mol site. Furthermore, the Boom Clay pore water has a negative $E_{\rm H}$ potential ranging between -328 and -224 mV.

Detailed observations show, however, a flat vertical trend, mainly expressed in the Na^+ , HCO_3^-

and Cl^- concentrations (see Honty *et al.* 2022*a*, fig. 8). These are explained by a simple out-diffusion starting at the time when the area of Mol emerged from the sea (Mazurek *et al.* 2009). Small second-order variations can be linked to the variable silt/ clay ratios in the specific layers.

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Based on the above-mentioned data set of pore water samples around the HADES URL, a 'reference composition' for Boom Clay pore water at the Mol site was defined. The reference composition corresponds to the average composition of the 195 pore water samples around the HADES URL and is indicated in Table 1 of Honty et al. (2022a) as the 'mean' composition. This reference Boom Clay pore water composition for the Mol site serves as an important input parameter in models simulating different scenarios of a repository life-time and longterm evolution of the host rock owing to, e.g., increased temperature, alkaline plume or seawater transgression. It is also needed in laboratory experiments (radionuclide diffusion and sorption experiments), and its composition serves as a basis to prepare synthetic pore water to be used in laboratory experiments.

The experimental data were also assessed by various geochemical modelling strategies and helped to update the reference pore water geochemistry model for Boom Clay (Wang et al. 2023). In the reference model, the most abundant pore water constituents, i.e. Na and HCO_3^{-} , are not constrained by mineral solubility or cation exchange but considered as system variables. Such an approach is justified provided that their concentrations were presumably affected by the infiltration of meteoric water from the overlying aquifer. All other elements are controlled either by mineral solubility (imposed by calcite, dolomite, siderite, pyrite, quartz, kaolinite and Mg-chlorite) or by cation exchange. Although both mineral assemblage and cation exchange models are able to predict the mean Boom Clay pore water composition, the mineral assemblage model seems to better explain the variations of the pore water composition at the formation scale.

The improvements also made it possible to monitor the impact of disturbances on the geochemistry. The extent of the oxidation zone around the HADES URL could be determined based on the pore water composition of piezometer filters installed at different distances from the HADES URL. The link between the spatial extent of oxidation and the extent of the EDZ (i.e. the fractured zone) was clearly demonstrated. By drilling with nitrogen drilling, it was possible to distinguish between the filters within the EDZ (and thus affected by oxidation) and those beyond the EDZ (not affected by oxidation). These findings were crucial to evaluate the natural variations of the Boom Clay pore water chemistry at the formation scale. This also allowed De Craen *et al.* (2008, 2011) to develop a conceptual model of the oxidation zone around HADES and identify oxidation as one of the main geochemical perturbations around the HADES URL.

Another disturbance that was and is being examined is the impact of increased temperatures on the Boom Clay geochemistry. This is done by extracting pore water from the filters installed around the PRACLAY Heater Test. These have been exposed to temperatures between 35.5 and 68.5°C. Pore waters were analysed for their chemical composition and gas composition. Also a microbial characterization was performed (Honty et al. 2022b). These analyses were compared with a predictive geochemical model simulating the Boom Clay pore water composition at increased temperature (Honty and Wang 2021). From the qualitative point of view, the preliminary results showed good agreement between the model and the empirical data for both the main constituents and key parameters, namely an increase in Na, alkalinity and pCO₂ and a decrease in pH as a function of increasing temperature. However, the geochemical model could be improved by accounting for the CO_2 produced by the thermal decomposition of the organic matter. This would result in a more realistic model and would allow a quantitative comparison. No clear correlation could yet be established between either increasing temperature and the total cell number or temperature and microbial activity. In the coming years, the scientific effort will be focused on both collecting more experimental data and improving the geochemical model at increased temperature.

Conclusions

The composition of the pore water of the clay host rock plays a crucial role in a series of processes relevant to the safety assessment. It is therefore crucial to characterize the pore water composition of the host rock and to gain insight into its possible evolution. The HADES URL has played an important role in characterizing the pore water of Boom Clay and made it possible to improve the methods and protocols for sampling and monitoring pore water.

These improvements, i.e. nitrogen drilling, the *in situ* circulation system, the implementation of operational procedures for pore water sampling, chemical and microbial analyses, and a data management system, marked a major step forward in the sampling and monitoring of pore water. They led to a better understanding of the Boom Clay geochemistry. The improved measurements and the more systematic analysis of pore water resulted in a larger and more reliable dataset. This dataset was used to update the reference pore water composition (Honty *et al.* 2022*a*) and geochemical model (Wang

et al. 2023). It also serves as input for geochemical models which assess the transport and long term behaviour of the radionuclides in both near and far fields of the repository.

Furthermore, the possibility to sample pore water and gas under *in situ* conditions and in real time also allowed the monitoring and evaluation of the impact of disturbances on the Boom Clay geochemistry. Examples of such disturbances are oxidation and a temperature increase in the host rock around a geological disposal system containing high-level waste. The latter disturbance is examined as part of the PRACLAY Heater Test (Chen *et al.* 2021; Dizier *et al.* 2021) in which the clay around the PRACLAY Gallery is heated. Piezometer filters around this gallery allow monitoring of the impact on the pore water composition.

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