25 years of cross-fertilization between HADES and Mont Terri rock laboratory

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Abstract: The collaboration between HADES and the Mont Terri rock laboratory started in 1995, when granite was considered the most suitable host rock for radioactive waste disposal in Switzerland. When an alternative host formation was looked for by NAGRA, the choice of clay as host rock became rapidly clear. It was then decided to build an underground research laboratory in the Opalinus Clay taking advantage of the excavation of a motorway tunnel crossing the Mont Terri anticline. Exchanges of knowledge and experience on the behaviour of argillaceous formations were focused on the feasibility of constructing a safe geological repository for high-level radioactive waste: from excavation and gallery lining techniques to geochemistry, diffusion of radionuclides and coupled thermo-hydro-mechanical processes. The research programme at Mont Terri and the growing numbers of partners from four up to nine countries worldwide led to successive extensions of the galleries. The scientific and technical advances made possible by the collaboration between both laboratories dealt with the development of common methods and joint experimental and modelling efforts. This review article summarizes the main scientific lessons learned during these exchanges, stressing the added values of the knowledge transfer between partners and the overall cross-fertilization between HADES and Mont Terri.

Supplementary material: Similarities and differences between Boom Clay in Mol and Opalinus Clay in Mont Terri are available at https://doi.org/10.6084/m9.figshare.c.6332962

During the last decades, generic and site-specific underground research laboratories (URLs) have been constructed worldwide in crystalline and sedimentary rocks. Besides the HADES URL, two major URLs in clay formations have been built and are presently operated in Europe, namely:

- the Meuse/Haute Marne URL, located in the Paris basin in France at a depth of −490 m in the Callovian–Oxfordian Clay Formation, and operated by ANDRA. More details can be found in one of the companion papers dealing with the development of the CIGEO project.
- the Mont Terri Rock Laboratory, located in the canton of Jura in Switzerland at a depth of −280 m in Opalinus Clay, operated by the Swiss Geological Survey at Swisstopo (Swiss Federal Office of Topography).

The very first hydrogeological investigations of Opalinus Clay at Mont Terri were performed by the Swiss National Hydrological and Geological Service (SHGN) in the reconnaissance gallery during the excavation works of the Transjurane motorway at the end of the 1980s (Tripet et al. 1990). The Mont Terri project, started in 1996, was aimed at assessing whether Opalinus Clay could be considered a safe alternative to crystalline rock for hosting a deep geological repository of high-level radioactive waste. Twenty-two partners from nine countries, including

the USA, Canada and Japan, are participating in the research at Mont Terri. By investigating processes closely related to the safety functions of a repository hosted in a clay formation, numerous experiments have increased our knowledge of the complex behaviour of clay formations in response to coupled thermal, hydraulic, mechanical (THM), chemical (C) and biological (B) processes. Innovative methods and commonly developed approaches successfully contributed to more finely characterize the THMC behaviour of clay formations: from a new tool for the undisturbed porewater pressure measurement to on-line measurement techniques of non-conservative chemical parameters of porewater (pH–E_h) and *in situ* diffusion experiments, without forgetting mine-by tests aimed at monitoring the hydro-mechanical (HM) response accompanying the excavation of galleries, or the characterization of the excavation disturbed zone (EDZ).

SCK CEN representatives, who initiated the works for the HADES URL in Belgium, were involved from the start of the Mont Terri project. Exchanges and cross-fertilization between both rock laboratories helped integrating available information and allowed us to evaluate the possibility of knowledge transfer for different clay materials from one clay formation to the other. The collaboration also contributed to building confidence in new experimental methods, monitoring techniques and the modelling works, in different multi-disciplinary fields. Integrating the huge collection of data allowed us to guide and to feed performance and safety assessment studies.

The collaboration initiated at Mont Terri was further fostered by international instances, such as the European Commission within its research framework programmes, NEA (OECD) with the 'Clay Club', and also IAEA in the frame of its URL network. It allowed us to perform large-scale *in situ* experiments to demonstrate the feasibility and the safety of waste disposal concepts by complementing and upscaling laboratory experiments in conditions representative of these of a future repository.

The Mont Terri Consortium was founded in 1996 with five first partners from four countries: with the French ANDRA, the Japanese PNC (now JAEA), the Belgian SCK CEN and the Swiss organizations NAGRA and SNHGS, the Swiss Geological Survey at this time. The Belgian Partner SCK CEN was thus present at the foundation of the Mont Terri rock laboratory and has been conducting experiments since 1996. All Mont Terri Partners benefited, and still benefit, very much from the Belgian Partner, as this latter had already excavated and operated a rock laboratory in a deep clay formation since 1980 (start of excavation works): the so-called HADES underground research laboratory (URL) in the Boom Clay Formation at the Mol site.

As early as 1995, workshops were held in Mol, where Belgian scientists shared their experiences learned from the Boom Clay with their Swiss colleagues. In Switzerland, experience for deep disposal of radioactive waste had mainly been gained from crystalline rocks. The Swiss scientists were therefore all the more surprised to learn how differently clays reacted hydraulically, mechanically and thermally depending on their composition and characteristics. The conclusion from these workshops was that the methods and techniques used in crystalline rocks (such as in granitic rock at the Grimsel Test Site in the Aar Massif in the central Swiss Alps) could not be directly transferred to a hard claystone. On the other hand, the methods used in the HADES URL could not be simply applied 1:1 to the Mont Terri site either. This is because on the one hand Opalinus Clay is a highly consolidated hard claystone while Boom Clay is more plastic, and on the other hand the stress regime of both sites considerably differs (thrusted and folded anticline structure v. simple horizontal clay layers). However, a consolidated hard claystone is, in respect with its hydro-mechanical behaviour, much closer to a plastic clay than it is to a crystalline rock. During the excavation works of the first niches in the security gallery of the Mont Terri tunnel in the spring of 1996, the knowledge obtained from the excavation of the HADES facility was therefore still – to some extent – applicable. Over the course of the Mont Terri project, all the partner organizations could, and still can, benefit from the knowledge and lessons learnt in HADES, taking into account the differences in geochemistry and hydro-mechanical behaviour.

Not only has Mont Terri benefited from HADES, but also vice versa, the Belgian organizations learned from Mont Terri. For instance, the current knowledge of SCK CEN and the chemical and microbiological expertise developed in the laboratories of SCK CEN were obtained and optimized during experiments at Mont Terri.

Organizations with a national clay programme have particularly benefited from the experiences of the HADES URL, not only saving time and effort, but also developing a more global and robust understanding of the clay behaviour between two formations with contrasted characteristics. The general integration of knowledge greatly benefited from the better understanding of the differences and similarities existing between highly and poorly indurated clay formations.

Overview of contributions of HADES to Mont Terri experiments

Since 1996, SCK CEN has been involved in experiments at the Mont Terri rock laboratory, together

with other Mont Terri Project Partners. Table 1 gives an overview of the last 26 years (1996–2022). It is noticeable that SCK CEN is mainly active in geochemical processes with a focus on porewater chemistry experiments and the interaction of clay with cement materials. Know-how transfer took place in the very early days with the so-called PP (porewater pressure) experiment. The experience gained in the HADES URL was directly incorporated into the design of a new porewater piezometer at Mont Terri. Special mention should be made of the Bitumen–Nitrate–Clay interaction (BN) experiment, which was precisely planned by the Belgian principal investigators and experiment delegates. Its design took into account the lessons learnt from previous geochemistry experiments at Mont Terri and HADES. This experiment has been running in the last 10 years and has produced excellent results. The Belgian nuclear safety authority FANC joined the Mont Terri project in 2015 and is mainly involved in the solute transport experiments such as the diffusion of radionuclides from a borehole into the Opalinus Clay under the influence of a thermal gradient. A selection of these experiments is presented in more detail in the section 'Examples of knowledge transfer between HADES and Mont Terri'.

Differences and similarities between Boom Clay and Opalinus Clay

Boom Clay and Opalinus Clay have quite contrasted characteristics and properties (soft v. hard clay formation) mainly inherited from their respective sedimentation and compaction histories (Mazurek *et al.* 2002, 2006; NEA, OECD 2005, 2022).

Geological settings and burial histories

The state of consolidation and cementation controlling the total porosity and the clay microstructure are very contrasted between Boom Clay (poorly indurated, 'plastic', or 'soft', clay with a very low carbonate minerals content) and Opalinus Clay (hard claystone with more sandy and carbonated facies). Boom Clay sedimented 32–28 Ma ago during the Rupelian stage of the Lower Oligocene Epoch in open marine conditions (50 to 150 m deep sea) and presently exhibits a quasi-horizontal stratification in the Mol area (clay slope *c.* 1–2% to the NE). Opalinus Clay was deposited as a shallower marine sediment 174 Ma ago during the Aalenian age of the Middle Jurassic. Due to the uplift of the Alps and the Jura folding, Opalinus Clay layers at Mont Terri are highly deformed in a thrusted anticline (folded Jura) and the clay layers dip from 30 to 50° to the SSE in the rock laboratory.

Boom Clay in Mol, where the Belgian URL is located, was never significantly buried (maximum −215 m), nor exposed at a temperature higher than 20°C, while Opalinus Clay submitted to the tectonic movements induced by the Alps orogeny, underwent a more pronounced diagenesis at 1350 m depth where it was exposed at a temperature of 85°C for several tens of millions of years during two successive events of burial and uplift (one during the Cretaceous Period, one in the Miocene Epoch) (Mazurek *et al.* 2002, 2006; Elie and Mazurek 2008; Bossart and Thury 2011). The different sedimentation conditions and burial histories explain many differences in the physical and chemical properties between the two clay formations. On one hand, this has complicated the transposition of the experimental measurement techniques between Boom Clay and Opalinus Clay, but on the other hand it has offered a unique opportunity to investigate a broad spectrum of physicochemical and geomechanical conditions. From the significant differences, but also the close similarities, observed between both formations, it was possible to better understand and to assess their contrasted behaviour (thermo-hydro-mechanical and geochemical) over a wide range of conditions relevant for the geological disposal of radioactive waste. It also allowed us to test and to compare a wide panel of different characterization approaches and modelling methods. This was invaluable to develop a more global, wider and robust understanding of key processes essential for the construction and the safety of a deep geological repository.

Basic physical and chemical properties

The Clay Club Catalogue of characteristics of argillaceous rocks, first compiled by Boisson at IRSN (NEA, OECD 2005) and recently updated by Kennell-Morrison at NWMO (NEA, OECD 2022) offers a convenient base to easily compare the main physical, geochemical and geomechanical properties of Boom Clay and Opalinus Clay along with several other clay formations also studied for the geological disposal of radioactive waste in other countries (NEA, OECD 2005, 2022). Both HADES and Mont Terri rock laboratories fruitfully contributed their high-quality data to the elaboration of the Clay Club Catalogue along with other research and waste management organizations in the frame of the international collaboration fostered by the Nuclear Energy Agency (NEA) of the OECD. It is worth mentioning that the Clay Club Catalogue was developed at the initiative of Marc Thury (1944–2021), former chief geologist at Nagra, founder and first chairman of the NEA Clay Club, and also the founder and first director of the Mont Terri rock laboratory (Thury 2016; Lambert 2021).

The high porosity (*c.* 38%), the high water content (*c.* 19 wt%) and the higher hydraulic conductivity ($K \sim 2\text{--}4 \times 10^{-12}$ m s^{-1}, perpendicular to

Table 1. *Mont Terri experiments in which the Belgian partners SCK CEN and FANC have been and are involved*

Abbr.	Title of experiment	Phase 1&2 1996/1997	Phase 3 1997/1998	Phase 4 1998/1999	Phase 5 1999/2000	Phase 6 2000/2001	Phase 7 2001/2002	Phase 8 2002/2003	Phase 9 2003/2004	Phase 10 2004/2005	Phase 11 2005/2006	Phase 12 2006/2007	Phase 13 2007/2008	Phase 14 2008/2009
BN	Bitumen–nitrate–clay interaction											ACNS	ACNS	ACINS
CI	Cement–clay interaction									N	N	N	AN	AIN
CI-D	Diffusion across concrete–clay interaction													
CS-C	CO$_2$-assessment of shale properties													
DI	Diffusion in claystone		AEINJS	AEINJS	AEINJS	AEINJS								
DR-B	Long-term diffusion													
DR-C	Porewater chemistry and diffusion													
EH	EDZ self-heating		ANS	ANS	ANS	NS	ANS							
FE-M	Long-term monitoring full-scale emplacement													
FM-A	Flow mechanism (fluid logging)	ANJS												
FM-C	Flow mechanism (tracer)	AEJNS	AEJNS	AEJNS	AEJNS	AEJS	AES	AES						
GD	Analysis of geochemical data											AENS	AENS	AENS
GT	Evaluation of gas transport models													
GP	Hydraulic and gas permeability	ANS	ANS	ANS	AS									
HT	Hydrogen transfer													ABN
MA	Microbial activity								ABCIN	ABCIN	ABN	ABN	ABN	ABNW
OP	Osmotic pressure	ANS	AINS	AINS	AINS	INS	INS	INS						
PC	Porewater chemistry								ABCJNS	ABCJNS	ABCJNS	ABCJNS	ABCJNS	ABCJNS
PC-C	Gas and porewater equilibration						ABENS	ABCJNS	ABNS	ABNS	ABNS	ABNS	ABNS	ABNS
PP	Porewater pressure	AS	AS											
WS-A	Groundwater sampling (*in situ*)	AENJS	AEINJS	AN	AN									
WS-B	Porewater sampling (laboratory)	ANJS	AEINJS	AN										

Abbr.	Title of experiment	Phase 15 2009/2010	Phase 16 2010/2011	Phase 17 2011/2012	Phase 18 2012/2013	Phase 19 2013/2014	Phase 20 2014/2015	Phase 21 2015/2016	Phase 22 2016/2017	Phase 23 2017/2018	Phase 24 2018/2019	Phase 25 2019/2020	Phase 26 2020/2021	Phase 27 2021/2022	Phase 28 2022/2023
BN	Bitumen–nitrate–clay interaction	AINS	AINS	AINS	AINS	AINS	AIS	AFIS	AFIS	AFIS	AFIS	AFIS	AFIMS	AFIMS	AFIMS
CI	Cement–clay interaction	AIN	ACINS	ACINOS	ACINOS	ACINOS	ACNOS	ACFNOS	ACFNOS	ACFNOS	ACFNOSW	ACFNORSW	ACFNORSW	ACFNORSW	ACFNORSW
CI-D	Diffusion across concrete–clay interaction									ACFNOSW	ACFNOS	ACFNORSWZ	ACFNORSWZ	ACFNORSWZ	ACFNORSWZ
CS-C	CO$_2$-assessment of shale properties							FT	FT	FT	FT	FT	FT	FT	FT
DI	Diffusion in claystone														
DR-B	Long-term diffusion		N	NW	DW	NW	NW	FNW	FNW	FNWT	FNRTW	FNRTW	FNRTW	FNRTW	FNRTW
DR-C	Porewater chemistry and diffusion										F	FMZ	AFMZ	AFHMTZ	AFHMTZ
EH	EDZ self-heating														
FE-M	Long-term monitoring full-scale emplacement ABDFGNPRW						DN		ABDFGNW	ABDFGNW	ABDFGNW	ABDFGNRW	ABDFGNRW		ABCDFGNRW
															ABCDFGNPRW
FM-A	Flow mechanism (fluid logging)														
FM-C	Flow mechanism (tracer)														
GD	Analysis of geochemical data	ANS	ANS	ANS	ANS	AENS	AENS	AEFNS	AEFNS	AEFNS	AEFNRSW	AEFNRSVW	AEFNRSW	AEFNRSW	AEFNRSW
GT	Evaluation of gas transport models									FH	FHR	FHM	BFHKMS	BFHKMS	BFHKMS
GP	Hydraulic and gas permeability														
HT	Hydrogen transfer	ABN	AN	ANW	ANW	ANW	AW	AFW	AFW	AFW	AFRW	AFRW	ABFRW	ABFRW	ABFRW
MA	Microbial activity	ABNW	ABNW	ABNW	ABNW	ABNW	ABNW	ABFNW	ABFNW	ABFNW	ABFNRWZ	ABFNRWZ	ABFNRWZ	ABFNRWZ	ABFNRWZ
OP	Osmotic pressure														
PC	Porewater chemistry														
PC-C	Gas and porewater equilibration	ABNS	ABNS	ABS	ANS										
PP	Porewater pressure														
WS-A	Groundwater sampling (*in situ*)														
WS-B	Porewater sampling (laboratory)														

Cross-fertilization between HADES and Mont Terri

Partners: A, ANDRA; B, BGR; C, CRIEPI; D, US DOE; E, ENRESA; F, FANC (FOWG*); G, GRS; H, ENSI (HSK); I, IRSN; J, JAEA; K, ETH; L, TOTAL; M, BASE; N, NAGRA; W, NWMO; O, Obayashi; P, BGE; R, RWM; S, SCK CEN; T, swisstopo; V, Chevron; Z, Helmholtz.
In total, there are 22 experiments, 11 of which have been completed and 11 of which are still ongoing. SCK CEN is mainly involved in geochemical experiments related to interactions with porewater and clay, but also with the interaction of cement materials with clay and its porewater. FANC is especially involved in molecular diffusion and solute transport experiments.

bedding) of the poorly indurated Boom Clay at −223 m in the HADES URL allow us to easily collect large quantities of clay porewater from boreholes equipped with piezometer tubing and porous filter screens. The lower porosity (11–16%), the lower water content (3.5–8%) and the lower hydraulic conductivity ($K \sim 6 \times 10^{-14}$–2×10^{-13} m s^{-1}, perpendicular to bedding) of the highly compacted Opalinus Clay initially made the possibility to directly sample porewater from boreholes questionable. However, large ascending inclined boreholes equipped with filter screens installed in the first excavated niches in 1996 rapidly proved it was possible to also directly collect porewater in a low-permeability formation as Opalinus Clay, even if the water flowrate is much lower than in Boom Clay.

At the notable exception of a much lower smectite content in Opalinus Clay, both formations exhibit similar clay mineralogy and secondary mineral assemblages. Opalinus Clay is also much richer in calcium carbonate and sand due to shallower sedimentation conditions reflected in its different facies (shaly, sandy and carbonate-sandy). Boom Clay which was never deeply buried also contains a higher level of organic carbon (0.3–2.4 wt%) than Opalinus Clay (0.2–1.2 wt%). Boom Clay organic matter (OM, kerogen still rich in humic and fulvic acids) is immature while OM of Opalinus Clay was submitted to 85°C for several tens of millions of years when the formation was buried at great depth. The chemical compositions of the porewaters are also contrasted: 0.015 M NaHCO$_3$ (pH $\sim$ 8.2–8.5) (De Craen *et al.* 2004; Honty *et al.* 2022) for Boom Clay while Opalinus Clay water essentially consists of half-diluted sea water (*c.* 0.3 M NaCl) (pH $\sim$ 7.2–7.5) (Pearson *et al.* 2003; Wersin *et al.* 2020, 2022). These different physicochemical characteristics are also reflected in the contrasted geomechanical properties of both clay formations: poorly or highly indurated clay (soft v. hard clay). More information is available in the Supplementary Material section allowing for the direct comparison of parameters dealing with the five following topics: (1) geological settings and burial histories, (2) main petro-physical parameters, (3) mineralogical composition, (4) main porewater characteristics and (5) main transport parameters (diffusion–advection). There are too many geomechanical parameters to list in the Supplementary Material but these can be accessed via the last version of the Clay Club Catalogue (NEA, OECD 2022) compiled by Kennell-Morrison (NWMO).

Examples of knowledge transfer between HADES and Mont Terri

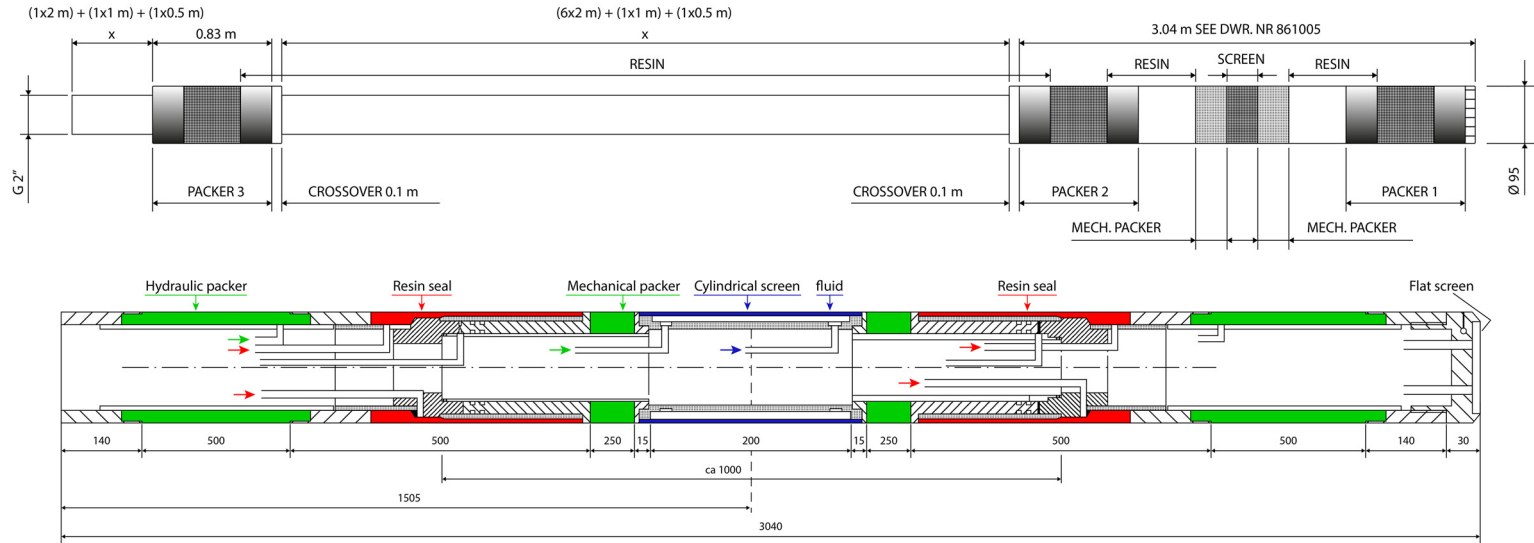The collaboration between HADES and Mont Terri covers areas as broad as geochemistry, diffusion and THM experiments, and has recently been extended to gas transport. First, we present the method developed to directly measure *in situ*, i.e. with minimal disturbance, porewater pressures in low-permeability clay formations ('Method for measuring porewater pressure' section). Second, we discuss THM experiments ('Time-dependent thermo-hydro-mechanical behaviour' section). Then, porewater chemistry and diffusion experiments are described in the 'Porewater chemistry experiments' and the 'Diffusion experiments' sections, respectively. Finally, cross-fertilization between experiments ongoing at Mont Terri (BN) and SCK CEN/HADES for assessing the nitrate reactivity in clay (nitrate released by the bituminized waste from the spent fuel reprocessing operations), is reported in the 'Nitrate reactivity in clay formations' section.

Method for measuring porewater pressure

The hydraulic porewater pressure is an important parameter to be measured for the characterization of clay formations. A good knowledge of the porewater pressure evolution is required to properly understand and model the hydraulic–mechanical processes in low-permeability clay formations. However, measuring porewater pressures in very low permeability clay layers reliably is a challenge. By the mid-1990s the techniques applied for this purpose in the HADES URL were considered reliable and robust. But as Boom Clay is a much more plastic clay than Opalinus Clay, the techniques from HADES had to be adapted before applying them at Mont Terri. Thanks to the experience acquired in HADES, it was possible to successfully adapt the techniques to the conditions encountered at Mont Terri in Opalinus Clay.

The aim of the porewater pressure (PP) experiment was to develop and validate piezometer equipment to reliably measure porewater pressures in a hard claystone with a very low hydraulic conductivity (typically in the range 10^{-12}–10^{-14} m s^{-1}). The requirements for such a system were threefold: (1) to avoid any leaks from the test interval or along the borehole wall, because in very low permeability media even very small leaks may lead to significant pressure drops; (2) to minimize the dead volume in the measurement section – the smaller the dead volume, the faster a hydraulic and chemical equilibrium is reached; and (3) to minimize the equipment's compressibility in the measurement section.

Based on these requirements, a porewater pressure piezometer was designed, assembled and tested before installation. Its design and principle are shown in Figure 1. The system constructed in collaboration with Solexperts was composed of a multi-packer system with four packers, one hydraulic and

Fig. 1. Principle of the porewater pressure piezometer specially designed and adapted for hard claystone. Above is the equipment installed in the BPP-1 borehole at the Mont Terri rock laboratory. A detailed longitudinal cross-section of the piezometer is shown. The test interval, consisting of a thin toroidal chamber equipped with a porous stainless-steel filter screen, is isolated by two sets of mechanical and hydraulic packers between which the annular space has been injected and tightly sealed with a very fluid epoxy resin.

one mechanical packer on each side of the toroidal test interval (or annular water chamber). The role of the mechanical packers is to keep the compressibility of the system low while the hydraulic packers ensure that the test interval remains hydraulically tight (no bypass water flow). In this double-packer system a very fluid epoxy resin (low viscosity type, freely flowing as water (dynamic viscosity typically of *c.* 1 centipoise as for water), allowing for simple gravity feeding) was injected between the hydraulic and mechanical packers in order to maintain a very tight long-term sealing. The test interval was lined with a cylindrical sintered stainless-steel filter, and its volume was kept as small as possible.

The first PP piezometer (BPP-1) was installed on 3 and 4 February 1997 in a 20 m deep horizontal borehole (101 mm diameter) in an unfractured zone of the shaly facies of the Opalinus Clay (Fig. 2). This PP piezometer contained two test intervals, one at a depth of 19.35 m and one at the end of the borehole, at 21.0 m. The most significant step of the installation procedure was the replacement of the air in the borehole by CO_2 to avoid trapping compressible and poorly soluble gases (N_2, Ar) in the system while also minimizing pyrite oxidation by O_2. After inflation of the packers, the air present in each test interval was first pumped out and replaced by much more soluble CO_2 for several times. Then an epoxy resin was injected between the hydraulic and the mechanical packers, and finally the test interval was filled with a best-guess artificial clay porewater (Pearson water) and rinsed several times to remove all the highly soluble CO_2 by dissolution. In this way, it was ensured that all the free volumes within the piezometer were totally filled with artificial porewater. It is important to note that the hydraulic pressure sensors of both test intervals were not directly installed in the borehole itself but inside a surface cabinet in the so-called PP niche, allowing an easy replacement of the sensors in case of failure. The rigidity and the tightness of the piezometer system allow the hydraulic pressure to be directly transmitted by the incompressible fluid completely filling the small diameter tubings without loss to the sensors installed in the gallery.

The results are shown in Figure 2. It is remarkable that the PP piezometer is still perfectly working after 24 years. The following three main episodes can be observed from the pressure curves: (1) two short pressure build-up periods in 1997, (2) the excavation of Gallery 98 in early 1998 with a significant pressure increase and (3) the slow decrease in the pressures in both test intervals, with cyclic fluctuations of the porewater pressures.
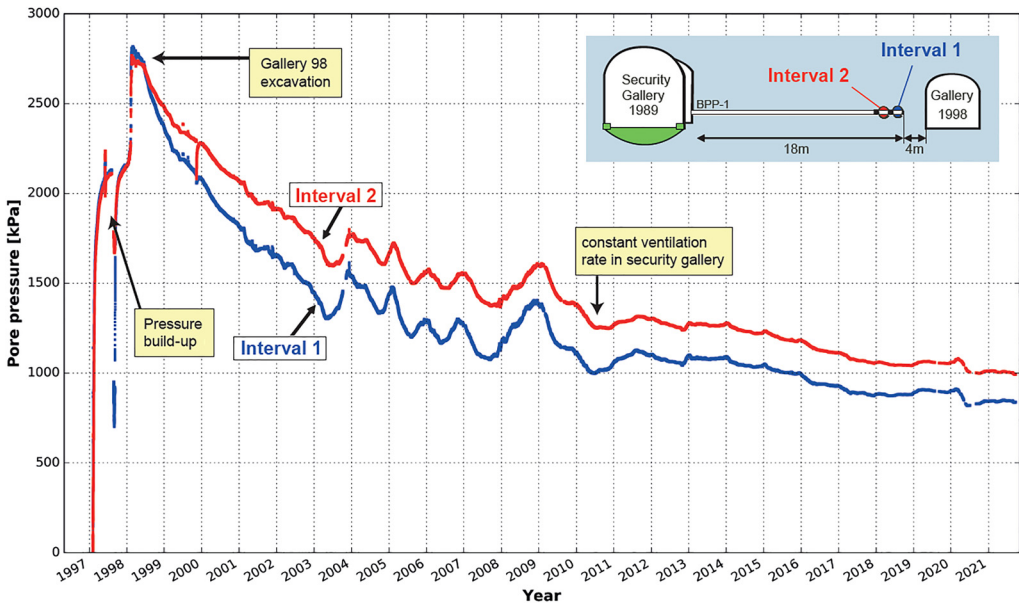

Fig. 2. Long-term monitoring of porewater pressures in the BPP-1 borehole. Three main events are visible: (1) pressure build-up just after installation in 1997; (2) hydro-mechanical porewater pressure response (increase) during the Gallery 98 excavation; and (3) slow pressure decrease until today. The pressure fluctuations observed between 2003 and 2011 were attenuated after the ventilation rate in the security gallery and the related seasonal changes of the climate conditions (temperature, relative humidity of air) were stabilized by the installation of airlocks at the tunnel entrances in 2011.

The episode of the Gallery 98 excavation can be nicely interpreted: it is a classical hydraulic-coupled process. Due to the stress re-distribution around the borehole during the excavation (blasting operations) of the tunnel, the mechanical deformations of the pore space around the test interval are reflected by an increase in the porewater pressure. Because the hydraulic conductivity is very small, it takes a while for the excess porewater pressure to dissipate again. These effects can be modelled very well and the hydraulic–mechanical characteristic parameters can be derived from them. The long-term decrease in pressure from 1998 until today is more difficult to explain and could be due to two processes: first, a slow clay desaturation, because water evaporates more quickly from the pore space into the tunnel than it flows in from the bedrock. Or, the second possibility, a mechanical de-consolidation of the Opalinus Clay around the Mont Terri motorway tunnel system, coupled with mechanical uplift and convergences, occurring over the long-term and continuing until today. Possibly, both processes are coupled with each other. The undulating pressure fluctuations are most likely due to seasonal variations in the tunnel climate conditions (temperature and relative humidity). These fluctuations were significantly attenuated when the tunnel air flow was significantly restrained by airlocks installed at the entrances of the security gallery in 2011. These results are consistent with the present knowledge acquired in the field of thermo-hydro-mechanical (THM) behaviour of clay formations and with the results of other mine-by tests performed during the next tunnel excavation phases (2004, 2008 and 2018) of the Mont Terri rock laboratory. The same porewater pressure variations (a first increase followed by a decrease) were also observed in 2002 in the poorly indurated Boom Clay in the HADES URL at Mol during the excavation of the connecting gallery with a tunnel boring machine equipped with a roadheader (Clipex mine-by test experiment).

To conclude we can say that the transfer of know-how from HADES to Mont Terri in terms of porewater pressure measurements was very fruitful. From the experience of HADES, a new piezometer could be developed that met the requirements for measuring porewater pressures in low-permeability hard claystone. Porewater pressure measurements in borehole are now routinely applied in different contexts in underground research laboratories, e.g. to assess various solicitations related to excavation works and thermo-hydro-mechanical perturbations. This principle was not only applied at Mont Terri in many other boreholes, but also in the French rock laboratory of ANDRA in Bure (Meuse – Haute Marne) and in the Japanese rock laboratory of JAEA in Horonobe (North of Hokkaido island).

Time-dependent thermo-hydro-mechanical behaviour

THM processes result from the coupling among temperature gradients (T), porewater pressure gradients with fluid flow (H) and mechanical stresses with deformation (M) (Li 2011; Tsang et al. 2012a, b). Due to the unavoidable underground excavations, the operation of the disposal facility (drainage and ventilation) and the thermal load (around 250 watt m^{-1}) generated by the waste, the favourable properties of the clay host rock for a radioactive waste disposal facility could change over time. Characterizing the evolution of the THM behaviour over time and/or solicitations is required to support the performance and the safety assessment studies. Regarding safety assessment, it is therefore important to identify and to quantify these perturbations and to assess their impact on the safety functions.

Mine-by tests, self-sealing observations (Bastiaens et al. 2007; Bernier et al. 2007) and THM experiments were performed both in HADES and Mont Terri underground laboratories allowing cross-fertilization on the understanding of key processes governing the THM behaviour of clays. This has been done among other things through collaborations in European projects and more specifically SELFRAC (fractures and self-healing within the excavation disturbed zone in clays; Bastiaens et al. 2007; Bernier et al. 2007) and TIMODAZ (Thermal IMpact On the DAmaged Zone around a radioactive waste disposal in clay host rocks; Li 2013).

The construction of the underground laboratory HADES started in 1980 (sinking of the first access shaft) allowed the building of a valuable geotechnical database. The extension in 2002 with a second shaft and a connecting gallery led to an accurate characterization of the EDZ generated by the excavation works. During the tunnel excavation, a progressive increase in the porewater pressure was observed by means of piezometers installed from the extremity of the existing gallery (Test drift) ahead of the excavation front followed by a sharp drop as the excavation front approached very closely towards the Test drift. One important finding was the occurrence of measurable hydraulic effects (the observed porewater pressure variations) at a distance of about 60 m (12.5 × tunnel diameter) ahead of the tunnel excavation. A network of conjugate fractures developed in the surrounding clay following a very characteristic herringbone pattern (chevron motif with V-shaped arrowheads developing along the excavation, or drilling, direction: >>>>>). This pattern is very similar to the fracture pattern observed at a smaller scale along boreholes as a result of the drilling (Fig. 3). The conjugate fractures are eye-shaped (flattened ellipse) around the boreholes as observed in their transversal cross-sectional plane. These
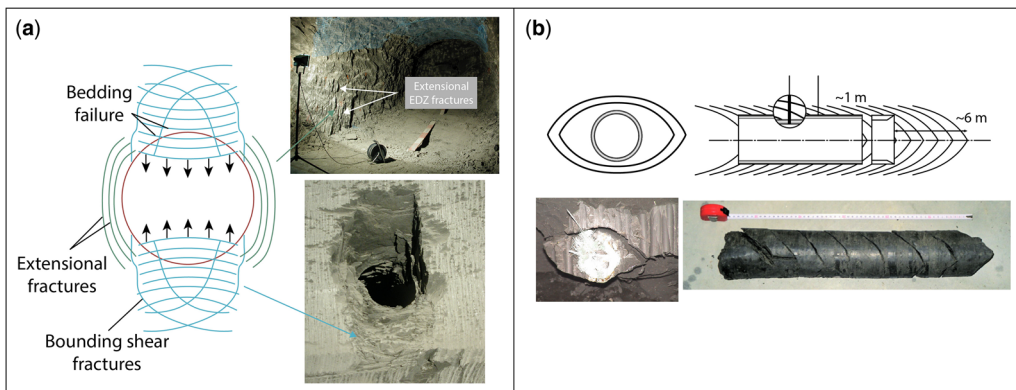
Fig. 3. Similar excavation damaged zone (EDZ) fracture pattern around galleries and boreholes observed in Opalinus Clay at Mont Terri (**a**) and in Boom Clay in HADES (**b**). Source: Blümling *et al.* (2007).

observations highlight the strong HM coupling in clay host rocks (Bernier *et al.* 2004).

At Mont Terri, the EDZ development observed is more complex due to the pre-existing anisotropies caused by diagenetic processes and a strong tectonic imprint. However, interestingly, the observed fracture patterns around the boreholes are eye-shaped similar to what is observed in Boom Clay (Fig. 3; Blümling *et al.* 2007).

The water retention properties of the host rock and the type of lining have been identified as key parameters controlling the rock desaturation from the drift upon ventilation (Barnichon 2012). Regarding the time-dependent deformation of clay, hydro-mechanical consolidation and creep are key processes. In both clay formations, a clear tendency for self-sealing has been observed, resulting in a significant reduction of the effective hydraulic conductivity in the EDZ. Boom Clay reacts very fast in this sense while Opalinus Clay requires more time (Bastiaens *et al.* 2007; Bernier *et al.* 2007; Bock *et al.* 2010). After several years and under saturated conditions, the maximum expected change from the initial hydraulic conductivity is maximally one order of magnitude higher than that of the intact rock (Blümling *et al.* 2007).

THM experiments performed in HADES (Atlas; Sillen *et al.* 2010) and Mont Terri (HE-E; Garitte *et al.* 2017) have allowed us to understand and model the coupling between temperature and the porewater pressure resulting from the differential thermal expansion of water and rock skeleton. The TIMODAZ project has shown that, while the hydraulic conductivity increases with temperature due to the decrease in water viscosity, the intrinsic permeability remains basically unchanged. This suggests that the permeability could decrease as a consequence of the thermoconsolidation (Sillen 2012). Large-scale THM tests are ongoing in both laboratories (PRACLAY in HADES; Dizier *et al.* 2021, Full-scale Emplacement (FE) experiment in Mont Terri; Müller *et al.* 2018) and should provide more information on the long-term THM processes and scale effects.

Despite the differences in their characteristics, the observed thermo-hydro-mechanical response in Boom Clay and Opalinus Clay presents similarities. Although the fundamental processes are to some extent the same, their relative importance and response rates can be very different. The differences are mainly caused by the higher compaction and thus the lower water content of the indurated clays and by the stronger bonding or cementation of clay particles. Taking note that different research teams, working independently and using different instrumentation devices, are able to point out similar processes builds confidence in the understanding of the potential THM perturbations and evolutions.

Porewater chemistry experiments

It is important to understand the porewater chemistry of the clay as it controls the chemical speciation, the solubility and the sorption behaviour of the dissolved radionuclides diffusing in the pore space. A good knowledge of the radionuclide speciation and the clay surface chemistry (cation exchange and surface complexation properties) is necessary for the preparation of migration experiments, their modelling and their correct interpretation.

Even if some experimental techniques may need to be adapted, the general methods applied for the characterization and the modelling of the clay porewater chemistry are the same, independently of the clay formation (Pearson *et al.* 2003; De Craen *et al.* 2004; Wersin *et al.* 2020, 2022; Honty *et al.* 2022). Boom Clay and Opalinus Clay are quite similar from the viewpoint of their clay mineral

composition (see Supplementary Materials: Table SM-3) even if Boom Clay is much richer in pure smectite content (14.2 wt%) than Opalinus Clay (c. 0 wt%) which was buried at great depth. Illite/smectite mixed layers are also more abundant in Boom Clay (15.3 wt%) than in Opalinus Clay (c. 10.0 wt%). Both clays strongly differ by their porosity (lower in the more compacted Opalinus Clay, c. 14% v. c. 34–38% in Boom Clay, cf. the NEA Clay Club Catalogue 2022; NEA, OECD 2022) and carbonate content (higher in the more cemented Opalinus Clay, 21.3 wt% v. 1.2 wt% only in Boom Clay, cf. the NEA Clay Club Catalogue 2022; NEA, OECD 2022). The accessory minerals are also the same (pyrite, calcite, siderite …) at the notable exception of celestite ($SrSO_4$) only present in Opalinus Clay because the sulfate content in the pristine Boom Clay porewater (0.6–2.3 mg SO_4^{2-} l^{-1}) is much lower than in Opalinus Clay (1700–2500 mg SO_4^{2-} l^{-1}). Boom Clay is also richer in organic matter (OM) and this latter is much less mature than OM in Opalinus Clay exposed at 85°C during several tens of millions of years when the formation was buried at great depth. The very immature kerogen of Boom Clay when submitted to a slight thermal stress at only 80°C releases CO_2 because of the fast decarboxylation of OM. The thermal decomposition of organic molecules containing unstable –COOH groups present in the thermolabile fraction of the Boom Clay kerogen is responsible for this CO_2 formation (Deniau 2002; Deniau et al. 2005; Lorant et al. 2008). The associated gas potential of Boom Clay is c. 49 mg of CO_2 per gram of organic carbon. This is no longer the case of Opalinus Clay already exposed to a much prolonged thermal stress at about the same temperature during its burial history. However, this temperature was insufficient to reach the oil window and in this way Opalinus Clay OM is considered by petroleum geologists as relatively immature (Mazurek et al. 2002, 2006; Elie and Mazurek 2008).

Organic matter thermal decomposition is not only one of the possible sources of the dissolved CO_2 present in the clay porewater but also likely at the origin of the unexpectedly high content of dissolved dinitrogen in the porewater (N_2). When Vinsot et al. (2008) measured the CO_2 in the Opalinus Clay in the PC-C borehole drilled under nitrogen gas they found an anomalously high partial pressure of N_2 in the batch gas samples analysed. This was first attributed to the N_2 drilling gas used to inert the borehole to avoid pyrite oxidation. In the frame of a later injection experiment with H_2 to study its fate in the clay formation (Hydrogen Transfer experiment (HT) started in 2009) another borehole was drilled with pure argon and H_2 injected along with noble gases (He, Ne, Ar) measured on line with a Raman spectrometer (Vinsot et al. 2014, 2017, 2018). It

was a great surprise to also obtain a pN_2 of about 3.55 bar (log pN_2: 0.55) in this experiment yet not contaminated in nitrogen gas by the Ar drilling gas (Vinsot et al. 2014, 2017, 2018; Wersin et al. 2020; Damiani et al. 2022). The presence of nitrogen gas (N_2) dissolved in significant quantities (2.2 mmol N_2 l^{-1}) in the clay porewater could be attributed to the thermal decomposition of natural N-bearing organic matter exposed to a thermal stress at 85°C during the burial history of the Opalinus Clay Formation. The mechanism of N_2 production/accumulation observed in the boreholes drilled in Opalinus Clay at Mont Terri could be the same as what is also sometimes observed in natural gas fields (Krooss et al. 1995; Littke et al. 1995) and clay minerals could be involved in adsorption and transformation processes of intermediate thermal degradation products (Charlesworth 1986). A pN_2 as high as 5 bar was also estimated by modelling the measured N_2 concentration (c. 3 mmol N_2 l^{-1}) dissolved in the porewater of the Callovo-Oxfordian Clay in the Bure URL (Damiani et al. 2022; Vinsot et al. 2022) but its exact origin is unknown as the Callovo-Oxfordian Clay Formation was less deeply buried than Opalinus Clay and therefore its organic matter exposed to a lower temperature (T_{max}: 50 ± 5°C according to Blaise et al. 2014) and a less pronounced thermal stress. Ammonium present in the smectite interlayer or a N_2 influx from the underlying geological formations might also have contributed to the N_2 accumulation in the clay porewater.

The near-neutral (Opalinus Clay, pH c. 7–8) to slightly alkaline (Boom Clay, pH c. 8.2–8.5) and strongly reducing (negative E_h) conditions, along with the pCO_2 in equilibrium with the clay porewater are important factors controlling the mobility and the retention behaviour of radionuclides dissolved in the porewater. In both clay formations, the great sensitivity of pyrite, Fe(II) minerals and organic matter, to oxidation by atmospheric oxygen (Baeyens et al. 1985a, b; Pearson et al. 2003) and the strong impact of the acidification by sulfuric acid produced by pyrite oxidation requires work under strictly anaerobic conditions without interruption in the whole operations chain. Sharing technical skills and practical experiences between the two underground laboratories to protect clay and porewater samples and for maintaining intact pristine reducing conditions proved to be essential to warrant the success of many geochemical experiments and to make serendipitous findings, such as the unexpectedly high partial pressure of dissolved N_2.

While sharing the same inherent sensitivity to oxidation, the undisturbed porewater chemistries of Boom Clay and Opalinus Clay are quite contrasted: Boom Clay water is typically fresh water with 15 mM $NaHCO_3$ and a high content of dissolved organic carbon (DOC: 80–160 mg C l^{-1}) while

OPA Clay water is essentially half-diluted seawater (0.3 ± 0.1 M NaCl) with a low DOC content (5–10 mg C l^{-1} DOM). In the poorly indurated Boom Clay Formation at the Mol site at limited depth (-180 to -280 m), the vertical chloride concentration profile is nearly flat with a constant concentration of 27 mg Cl^- l^{-1} (7.6×10^{-4} mol Cl^- l^{-1}) of chloride because most of the NaCl from ancient seawater has already diffused out of the Boom Clay Formation into the surrounding fresh aquifers (Neogene and under Rupelian aquifers) during the Quaternary Period after the area finally emerged from the sea about 2 Ma ago (Vandenberghe 1978; Mazurek *et al.* 2009, 2011; Vandenberghe *et al.* 2014). At Mont Terri, the situation is different and more complex because of its lower total porosity and lower effective diffusion coefficients (D_e) for solutes and because the fresh water circulation in the surrounding limestone aquifers (Dogger limestone above Opalinus Clay and older Liassic Gryphaea limestone in the centre of the anticline) started only relatively lately in the anticline history related to the Jura folding (Bossart and Wermeille 2003; Mazurek *et al.* 2009, 2011). As a result, a very characteristic chloride concentration profile has developed through the whole Mont Terri anticline, with a higher salinity close to the older clay layers located near the centre of the anticline (Pearson *et al.* 2003; Wersin *et al.* 2020, 2022). Both chloride profiles were modelled by Mazurek *et al.* (2009, 2011) (CLAYTRAC project of the NEA Clay Club) with those of seven other sites to assess the diffusion of natural tracers dissolved in the clay porewater as the dominant transport process across the entire clay formation using transport parameters derived from laboratory or *in situ* tests.

SCK CEN developed different systems to directly measure on-line pH and E_h values by means of flow-through cells directly installed on the water tubing of piezometers and equipped with glass and platinum electrodes with their own internal reference electrode of the Ag/AgCl type. This way, pH and E_h were first measured on line at atmospheric pressure in 1990 in the HADES URL on the Cerberus experiment aimed to study the effects of heat ($T = 80°C$) and radiation (10 000 Ci of ^{60}Co) on the near-field clay (De Cannière *et al.* 1996; Noynaert *et al.* 1998, 2000). The clay water was directly flowing along the hydraulic gradient from a piezometer through the measurement cell installed in the gallery (once-through flow). This experimental setup was the simplest but its main disadvantage was the CO_2 degassing from water and the CO_2 loss to the atmosphere affecting the pH measurements (with pH values higher than the real *in situ* value).

At the same time, in the early 1990s, in the frame of the Archimède European project (Griffault *et al.* 1997) aimed to characterize Boom Clay (mineralogy, porewater chemistry and microbiology), CEA (Pitsch *et al.* 1995*a*, *b*) tested an optode at the *in situ* hydraulic pressure (up to 22.3 bar, the hydraulic pressure in Boom Clay at -223 m) to overcome the problem of CO_2 degassing. An optode, standing for 'optical electrode', simply consists of a spectrophotometer directly measuring the colour change of a pH indicator impregnating the tip of an optical fibre. As the optical fibre can operate without problem at elevated hydraulic pressure, the optode was simply inserted in the filter screen located at the extremity of a piezometer (30 m away in the clay formation). The water tubing was hermetically closed and pH measurements were performed during the water pressure recovery (a few days). Without CO_2 loss, a pH of 8.2 was measured for the first time with the CEA optode, a value lower than the 8.5 usually measured in the laboratory at atmospheric pressure in already partly degassed Boom Clay water.

During the 1990s–2000s, the collaboration and the regular scientific exchanges on clay porewater with CEA and IRSN (Pitsch *et al.* 1995*a*, *b*; Beaucaire *et al.* 2000) continued while SCK CEN strived to improve its own pH–E_h system and to find a way to operate the flow-through cells at *in situ* pressure avoiding CO_2 degassing. The main technical challenge was to find water pressure-resistant electrodes (up to 22.3 bar). Different solutions were envisaged and many types of electrodes tested until polymer-filled Xerolyt electrodes (Ingold, Mettler Toledo) able to withstand high water pressure were successfully tested. To maintain the *in situ* hydraulic pressure while water could still flow around the electrodes, the flow-through cell was installed in a closed loop water circuit equipped with a gear-wheel recirculation pump and connected to the piezometer filter screen via two tubings. Once operating with brand new electrodes at *in situ* water pressure, this closed loop system allowed us to measure the same pH value as with the CEA optode. However, due to the continuous KCl leakage from the reference compartments of the electrodes and their possible poisoning by sulfide, if not replaced, or calibrated, in due time, the reference electrodes suffered a serious drift and the apparent pH value considerably increased with time.

In 2001, SCK CEN joined the Porewater Chemistry (PC) experiment at Mont Terri aimed at characterizing the clay porewater under undisturbed and pristine conditions and installed an improved version of its pH–E_h on-line measuring system (Wersin *et al.* 2011*a*). The components of the system operating under inert atmosphere (argon gas to avoid atmospheric oxygen because of the E_h measurements) in the surface cabinet were all made from polymers only (metal-free) in order to eliminate reducing artefacts caused by stainless steel for the redox

measurements (Fig. 4). After a few months, the clay water composition and the pH–E_h measurements became puzzling (Pearson *et al.* 2011; Wersin *et al.* 2011a). It became rapidly clear that the PC experiment was affected by a strong microbial reducing perturbation, i.e. sulfate-reducing bacteria (SRB) and methane-producing bacteria (MPB) were active in the system (Stroes-Gascoyne *et al.* 2011). The objective of the PC experiment was then reoriented towards the bio-geochemical characterization, the modelling and the understanding of the microbial perturbation. Its impact on the porewater chemistry, the interactions with the surrounding clay (Koroleva *et al.* 2011; Tournassat *et al.* 2011) and the safety components of the engineered barriers of a geological repository (Wersin *et al.* 2011b) were studied in detail. It was found that an unknown source of organic carbon was fuelling the microbial activity. GC-MS analyses of the different polymeric materials (PEEK, PE, PA and PU) could not identify a notable source of organic carbon in the fabrication materials (De Cannière *et al.* 2011). Acetone, initially suspected because it was used to clean the polyethylene (PE) porous filter before use, could only have partly contributed to fuel bacteria in the first few months of the PC experiment. It was only at the end of the PC experiment that the reason of the microbial perturbation was discovered. The polymer-filled Xerolyt electrodes did not contain pure polymer filling material as initially supposed,
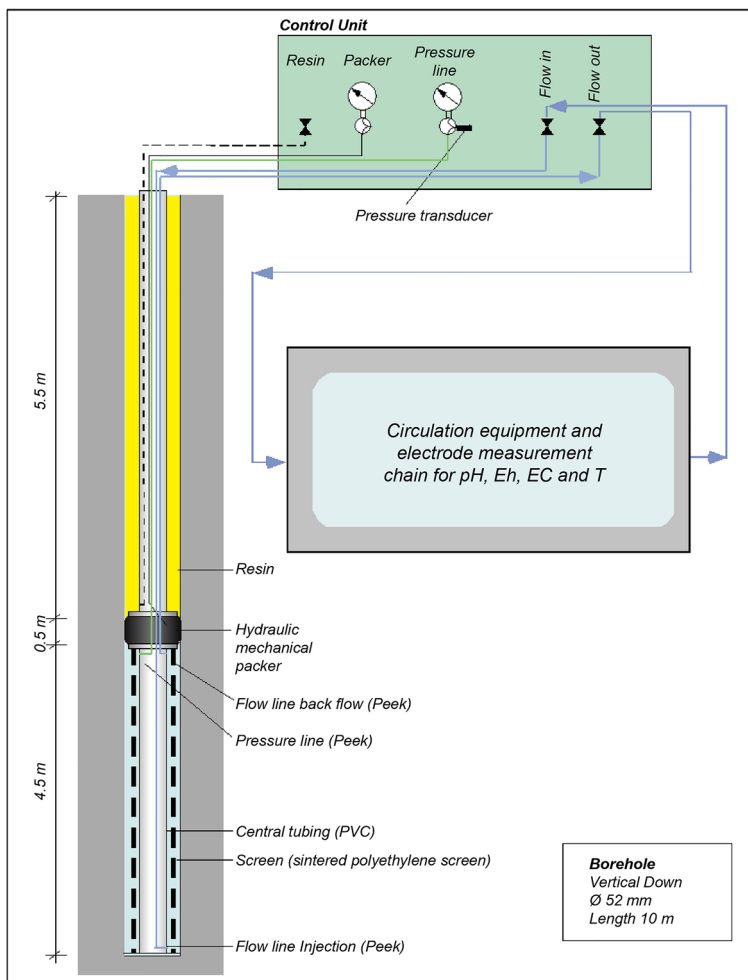

Fig. 4. Setup of the Porewater Chemistry (PC) experiment made at Mont Terri from 2002 to 2007: diffusive equilibration of artificial porewater with the host rock and on-line measurement system of pH, standard redox potential (Eh versus the standard hydrogen electrode), electrical conductivity (EC) and temperature (T). The experimental setup closely resembles that of the first *in situ* diffusion experiments (DI, DI-A, DI-B).

but also 50 wt% of glycerol. The high leak rate of the reference electrodes was responsible for the release of glycerol along with KCl in the water of the close loop circuit (De Cannière *et al.* 2011). With a total of 12–15 Xerolyt electrodes used during the 5 years of the PC experiment, the glycerol inventory available to fuel microbial activity was significant. The lesson learnt from this unexpected perturbation was that these pH–E_h electrodes cannot stay immersed in the water circuit for a continuous measurement during a long time. Discontinuous measurements with electrodes isolated in an automatically purgeable and rinsable storage cell would have been preferable. An alternative was to use very low leaking electrodes as adopted later in the BN experiment in Mont Terri (see the 'Nitrate reactivity in clay formations' section). If no sufficient precautions are taken, microbes can easily develop in experiments and alter their results, but more importantly, the role of microbial activity should be systematically considered in all geochemical experiments to question the validity of their design and their results. The same also applies for the construction and operation of a deep geological repository. In the case of backfilling of the disposal galleries with a buffer material that is of too low density, or if macro-voids still subsist, no space and water restrictions will limit the development of microbial activity around the waste, or in the engineered barrier system. On the one hand microbial activity could promote favourable redox processes leading to a lower oxidation state for radionuclides, contributing so to increase their retention (precipitation and sorption), but on the other hand the presence of microorganisms may also contribute to accelerate the degradation of the performance of the engineered barriers (Stroes-Gascoyne *et al.* 2011; Leupin *et al.* 2017). This is particularly a concern for the corrosion of metallic barriers, as sulfide and thiosulfate anions produced by SRB are known harmful species increasing locally the corrosion rate of the metallic packages.

Another porewater chemistry experiment performed at Mont Terri was the PC-C experiment (Vinsot *et al.* 2006, 2008), which initially aimed to determine the pCO_2 in Opalinus Clay with on-line FTIR (Fourier transform infrared spectroscopy) measurements and independent analyses on gas samples. After the first phase dealing with gas analysis and the subsequent removal of the gas measuring system, the PC-C test interval was completely saturated with water and a once-through flow cell equipped with pH and E_h electrodes was installed in the gallery at the end of the water lines. This experimental setup presents the main advantage of avoiding continuously recirculating any contamination of the clay water by the chemicals (KCl and organic matter) leaking from the electrodes. To limit the CO$_2$ degassing to the atmosphere, a special system exerting a counter hydraulic pressure adjusted by means of a controlled piston was also installed. This made it possible to achieve undisturbed conditions and reliable pH and E_h measurements.

Coming back to the HADES URL and Boom Clay, many attempts were made to directly measure the *in situ* pCO_2 value in equilibrium with the porewater of the piezometers. The principle consisted in sampling and analysing the gases dissolved in the porewater coming from the clay formation after they progressively accumulated in the headspace of a stainless-steel container initially filled with pure argon (Mijnendonckx *et al.* 2019; Honty *et al.* 2022). The water seeping from the clay formation was continuously recirculated at *in situ* hydraulic pressure in a close circuit equipped with glycerol-leaking pH–E_h Xerolyt electrodes. The results of the measurements were also unexpected and puzzling: no CO_2 could be detected by gas chromatography, but only methane (CH_4) was present (Mijnendonckx *et al.* 2019). As in the Porewater Chemistry (PC) experiment at Mont Terri, in the absence of space and water restrictions, MPB thrived and prevented the attempts of pCO_2 measurement from piezometer water in HADES. However, reliable pCO_2 values were obtained by Gaucher *et al.* (2010) by direct CO_2 measurement on clay cores immediately packed after drilling in evacuated and tight stainless-steel containers following a method first developed at SCK CEN by Henrion *et al.* (1985) on Boom Clay. In their comparison exercise of pCO_2 measurements in the four main deep clay formations presently studied in Europe for geological waste disposal (at the Mol, Mont Terri, Bure and Tournemire sites), Gaucher *et al.* (2010) obtained values of $\log_{10}(pCO_2, bar)$ of -2.33 to -2.15 for Boom Clay in HADES and of -3.07 to -2.12 for Opalinus Clay in Mont Terri.

For years in the HADES URL, the same glycerol-containing Xerolyt electrodes were permanently installed on line in many piezometers, continuously fuelling MPB, and so preventing any reliable CO_2 measurements. The lesson learned is that in the absence of space and water restrictions (i.e. presence of free water in tubings and containers), if sufficient organic carbon is available, bacteria thrive and their metabolic activity inevitably affects long-term geochemical measurements (Stroes-Gascoyne *et al.* 2011). Recirculation systems continuously operated in a closed loop for months or years are very sensitive to microbial perturbations. The addition of biocides or microbial inhibitors such as sodium azide (NaN_3) during geochemical measurements to warrant abiotic conditions, especially for long incubation periods, is not an alternative as they can also interfere and strongly disturb the experimental results (Hendrix *et al.* 2019).

Openly discussing and questioning the reasons of unexpected results during the many scientific and technical exchanges between the HADES URL and the Mont Terri rock laboratory has been very fruitful. These reciprocal and constructive exchanges have definitely helped to identify the root causes of unexpected experimental artefacts and to resolve many technical limitations. HADES and Mont Terri have driven many monitoring and method developments (choice of electrodes, on-line measurement techniques, etc.) to directly characterize *in situ* non-preservable geochemical parameters (pH, E_h, pCO_2). These developments and especially the lessons learned on the need to take into account from the very basic design of experimental setups the effect of microbial activity and related reducing perturbations on the geochemical measurements represent an important step in the learning process and have helped the scientific community to design more appropriate and robust techniques for successful geochemical field work.

Diffusion experiments

Boom Clay and Opalinus Clay have many favourable properties in common to limit and slow down by diffusion and sorption the release of radionuclides out of a radioactive waste repository (low hydraulic conductivity and high sorption capacity for radionuclides) but also exhibit significant differences in their porosity and geomechanical behaviour due to their different level of compaction and cementation (soft v. hard clay).

Since the end of the 1970s and the construction of the HADES URL (1980–81), the radionuclides transport controlled by diffusion in the poorly permeable clay formations and their sorption onto the clay minerals have been identified as the main processes limiting their release from the host rock to the biosphere (De Marsily *et al.* 1977; Put and Heremans 1977; Baeyens *et al.* 1982; Henrion *et al.* 1985). Different types of laboratory and *in situ* experiments have been successfully applied to study radionuclide diffusion in both clay formations, and when necessary adapted as a function of their geomechanical properties: more plastic or more brittle.

Because of the very fast natural convergence of the plastic Boom Clay around the piezometer casings installed from the HADES URL, after a few months of reconsolidation of the clay around a borehole, a preferential path for porewater and radionuclides along the casing of a piezometer is no longer observable. The annular space of boreholes being well sealed, it is not necessary to install packers on piezometers tubings emplaced in Boom Clay. Two main types of *in situ* migration experiments have been installed from the HADES URL: small-scale

percolation experiments with sorbing tracers and large-scale diffusion tests with non-sorbing tracers.

Small-scale percolation experiments were first performed *in situ* with strongly sorbing tracers (Cs^+, Sr^{2+}, Eu^{3+}, Am^{3+} and $Tc(IV)$) with well-preserved Boom Clay cores reinstalled in contact with the clay formation after their labelling with the radionuclide of interest. A paper filter impregnated with the tracer was sandwiched between two back-to-back clay cores in the surface laboratory. The whole was closely assembled between two porous filters in a stainless-steel percolation cell under anaerobic conditions. The percolation cell was mounted at the extremity of a long metallic tube left open at the upstream side of the cell in direct contact with the clay formation and equipped with a water tubing on the downstream side (other side towards the gallery) to allow us to sample the porewater percolating through the clay under the effect of the hydraulic gradient existing around the gallery. The percolation cells were reinstalled in direct contact with the pristine clay of the formation at the end of a borehole far away from the gallery (Put *et al.* 1988; De Cannière *et al.* 1996). After monitoring of the radioactive tracer in the percolating porewater, the cell was retrieved from the borehole and the tracer profile was measured in the clay core. The main advantage of this approach is the availability of fresh porewater during relatively long-term experiments. It allows us to preserve undisturbed geochemical conditions (pH, E_h, pCO_2, T) in the small clay cores (Put *et al.* 1988). The experimental conditions are thus closer to these expected in the far field of a repository at the notable exception of the hydraulic gradient forcing the water to flow through the clay cores.

The objective of the small-scale *in situ* percolation experiments made on intact Boom Clay cores was to verify under undisturbed *in situ* conditions the results of the experiments performed in the surface laboratory. Beside the first *in situ* percolation experiments made under undisturbed conditions with Cs^+, Sr^{2+} and Eu^{3+}, the effects of heat ($T = 80°C$) and radiation (gamma source of 10 000 Ci of ^{60}Co) on the chemistry of ^{241}Am (trivalent actinide sensitive to complexation by dissolved organic matter) and ^{99}Tc (artificial redox-sensitive element with a chemical behaviour resembling that of manganese and rhenium) were studied in the frame of the so-called Cerberus test, an integrated multidisciplinary experiment, aimed at investigating the thermal and radiation effects on the clay near field around an HLW canister (De Cannière *et al.* 1996; Noynaert *et al.* 1998, 2000).

Several large-scale and long-term diffusion experiments with direct *in situ* injection of non-sorbed tracers (tritiated water or HTO, $^{125}I^-$, ^{14}C-labelled HCO_3^- and ^{14}C-labelled organic matter)

were also performed in the Boom Clay Formation (Monsecour *et al.* 1991; De Cannière *et al.* 1996; Aertsens *et al.* 2013; Weetjens *et al.* 2014). Their main aim is to upscale laboratory migration experiments performed at the centimetre scale on small clay cores to the metre scale in the clay formation (verification of possible spatial heterogeneities in the clay and representative elementary volume (REV) of the cores), and to validate predictive model calculations for the migration of conservative tracers in a deep clay formation.

The first large-scale *in situ* diffusion experiment with HTO was installed in 1988 behind the large concrete plug (CP-1) closing the northern extremity of the HADES URL in the cast iron gallery (Monsecour *et al.* 1991). This experiment consists of a so-called piezometernest equipped with multiple porous filter screens (sintered stainless steel) distributed on the length of a metallic tubing at regular interval (1 m) and installed in one single borehole. Each metallic sintered filter surrounds small volume toroidal chambers equipped with one or two water tubings to sample porewater. The inner central cavity of each chamber allows us to accommodate the passage of the water tubings coming from the other filters installed further on the tube. Tritiated water (HTO) was injected through the central filter and its migration remains regularly followed by sampling the porewater in the neighbouring filters. In contrast to Mont Terri where diffusion experiments with radionuclides are performed below the exemption limits, HADES having the status of a nuclear controlled zone located below the SCK CEN site, it allowed the injection of 20 mCi of HTO, which enabled the follow-up of the experiment during several decades at the scale of several metres.

The other large-scale diffusion experiments started later during the 1990s are based on the same principle. The experiments performed with $^{125}I^-$ in the vertical and horizontal direction in the ring R-41 of the Test Drift and the 3D-configuration piezometer system (co-injection of HTO and ^{14}C-labelled HCO_3^-) are also intended to confirm under undisturbed *in situ* conditions, and at a larger spatial scale, the anisotropy of diffusion of conservative tracers previously determined on small Boom Clay cores in the surface laboratory (De Cannière *et al.* 1996; Aertsens *et al.* 2013; Weetjens *et al.* 2014).

Joining the Mont Terri project in 1995 was a unique and fruitful opportunity to exchange experiences and to learn from each other. Until the end of the 1980s, Boom Clay was the only deep clay formation investigated as a potential host rock while granite and salt rocks were the favourite options in many other countries. In 1996, the HADES team joined the Mont Terri technical discussions to design and construct the first *in situ* diffusion experiments

(DI) (Palut *et al.* 2003) in the shaly facies of Opalinus Clay at the north of the rock laboratory, and the FM-C (Flow Mechanism tracer) experiment in the main fault zone.

The main question first addressed was the feasibility of the transferability of the diffusion techniques used *in situ* in a soft clay formation to a hard claystone. Because of the technical constraints imposed by the geomechanical and hydraulic properties of Opalinus Clay, it becomes rapidly evident that the system used to inject tracers and to monitor their diffusion into Boom Clay was not applicable to Opalinus Clay.

The lower porosity and the >10 times lower hydraulic conductivity of Opalinus Clay (10^{-13} to 10^{-14} m s^{-1}) and its stiffness prevent the same type of diffusion experiments being performed in the Mont Terri rock laboratory than in Boom Clay from the HADES URL. The insufficient natural convergence of Opalinus Clay requires the use of packers to hydraulically isolate the test interval while the direct sampling of sufficient volumes of porewater is not possible because of the hydraulic conductivity of the clay, which is too low. A supplementary legal constraint to be respected in the non-nuclear environment of Mont Terri was also a much lower maximal allowed activity for the use of radiotracers in the *in situ* experiments. For these reasons, it was necessary to develop in close co-operation with all the partners and contractors of the DI project a new type of diffusion experiment also further used for the DIR diffusion experiments in the Callovo-Oxfordian Clay in Bure (Meuse – Haute Marne, France) (Delay *et al.* 2007; Dewonck *et al.* 2010).

The principle of the *in situ* diffusion experiments at Mont Terri is the following: an artificial porewater (APW) solution spiked with a cocktail of tracers with a known initial concentration (C_0) is continuously recirculated through the porous filter screen of the injection interval. The concentration of the tracers in the water reservoir in the gallery is regularly measured to follow the evolution of their C/C_0 ratios as a function of time during one or two years. At the end of the experiment, the downhole equipment is removed from the borehole and the remaining cavity mechanically stabilized with a mixture of quartz powder and epoxy resin. Then, the clay surrounding the injection filter is recovered by overcoring. The clay of the overcore is cut in thin slices in the radial direction to determine the tracers' diffusion profiles as a function of the distance from the source. Appropriate cutting tools are used depending on the diffusion depth of each tracer. While chisels, hammers and saws are sufficient tools for non-sorbed tracers migrating relatively long distances (10–20 cm), for strongly sorbing tracers it was necessary to develop an innovative abrasive peeling technique appropriate for the millimetre scale (Van Loon and Eikenberg

2005; Van Loon and Müller 2010, 2014). After analysing the data obtained from the different clay diffusion profiles and reconciling them with the tracer concentration evolution with time in the recirculated water, the diffusion parameters are determined by modelling.

The special overcoring technique developed at Mont Terri has never been implemented in the HADES URL for two reasons:

(1) The small-scale percolation experiments confined and protected inside their robust stainless-steel cells could be easily retrieved by much more simple overcoring and without risk of losing them.

(2) The high porosity (*c.* 38%, as determined with HTO migration experiments), the high water content (*c.* 19 wt%) of Boom Clay and the large hydraulic head around the HADES gallery at −223 m depth allow us to easily sample porewater for analysing the dissolved non-sorbing tracers without the need for an overcoring for extracting them from the solid clay.

Many diffusion experiments in Opalinus Clay have been successfully performed with overcoring and the diffusion and sorption parameters of the injected radionuclides were determined by modelling the experimental data (Leupin *et al.* 2018): DI (Palut *et al.* 2003), DI-A1, DI-A2, (Wersin *et al.* 2004), DI-B (Yllera *et al.* 2004), DR (Leupin *et al.* 2013; Gimmi *et al.* 2014), DR-A (Soler *et al.* 2019). However, an overcoring always remains a risky operation and an experiment can be entirely lost at the last minute, as was the case with the overcoring of the Cement Water (CW) experiment in 2002 and also for two of the DIR diffusion experiments made at Bure. Indeed, sometimes, the overcoring tool can unexpectedly behave like a grinding coffee machine and the overcore aspired as dust into the vacuum cleaner equipment.

The FM-C experiment performed with dissolved helium injection and a mass spectrometer in the main fault zone indicated that the hydraulic conductivity in the main fault was of the same order of magnitude as in the intact rock matrix (Gómez-Hernández and Guardiola-Albert 2004; Bossart and Thury 2011). This is explained by the present geological settings of the Opalinus Clay Formation in the Mont Terri anticline and by the regional stress and the weight of the 250–300 m thick overlying terrains compressing the inclined clay layers together and closing the fissures. Indeed, the Mont Terri anticline is submitted to the thrusting action exerted by the Jura folding and the Alps uplift. The main fault, recognizable thanks to the presence of slickensides along the fractures surface, clay gouge and scaly clay, is presently inactive and watertight and the characterization of its tectonic structure and the microstructure of its pore space has been the subject of many works (Jaeggi *et al.* 2018; Laurich *et al.* 2018; Orellana *et al.* 2022). As the clay layers are submitted to important compression forces inside the anticline structure, the main fault is sealed and remains watertight. It is noteworthy to mention that in other clay formations, such as in the Toarcian–Domerian Clay at the IRSN experimental station in Tournemire (Millau, Aveyron, France) water-conductive fractures remain open and flowing water can even be sampled because of their extensional state related to the ancient tectonic evolution of the clay massif (Constantin *et al.* 2002, 2004).

Recent or new diffusion experiments (DR-B, CI-D, DR-C, DR-D and DR-E, by chronological order of implementation) are still ongoing, or being prepared, at Mont Terri, using the latest technical developments. The DR-B diffusion experiment is a long-term passive experiment with a large injection chamber containing 150 l of 2M stable NaI (Jaquenoud *et al.* 2021). The diffusion of NaI in the Opalinus Clay and the exchange of the Na^+ cations with these of the clay minerals (such as Cs^+) are followed by means of an X-ray fluorescence (XRF) probe inserted at regular interval in two vertical observation boreholes parallel to the main injection borehole. X-ray fluorescence of minor and trace elements (such as Cs, Ca, Sr, Ba, REE, etc.) allows a precise mapping of the clay layers and of the long-term NaI migration plume. The CI-D experiment is also in progress to characterize the diffusion of HTO and $^{36}Cl^-$ in the altered skin present at the interface between cement and clay (CI experiment) to assess porosity changes (i.e. the possible clogging of the pores at the interface). DR-C, a new diffusion experiment initiated by FANC, is starting to investigate the diffusion of radioactive tracers and stable isotopes in a thermal gradient to simulate the migration of radionuclides during the thermal phase of a HLW repository after the early failure of a spent fuel canister. Finally, the DR-D diffusion experiment led by the Helmholtz Association is aimed at investigating the heterogeneity of the sandy facies near the Passwang Formation (in the southern zone of the laboratory) after a detailed geophysical characterization, while DR-E will be a long-term diffusion experiment installed in the Mont Terri main fault zone to confirm its transport parameters for performance and safety assessment studies.

The different states of consolidation and cementation observed between Boom Clay and Opalinus Clay and their total respective porosity are contrasted. This has complicated the transposition of the experimental diffusion techniques from Boom Clay to Opalinus Clay. However, the chemistry and the migration behaviour of radionuclides and stable tracers are governed by the same physico-chemical processes and interactions. In these

compact and low-permeability deep clay formations, the radionuclide migration is limited by diffusion while strongly reducing and near-neutral to slightly alkaline chemical conditions maintain redox-sensitive radionuclides in their lowest oxidation states in which they are less mobile (i.e. poorly soluble and strongly sorbed onto the clay). On the one hand, the diffusion of anions is restrained by Donnan exclusion (anion exclusion) because the diffusion accessible porosity of anions (corresponding to the 'geochemical porosity' of Pearson (1999) and Pearson *et al.* 2003) is about half that of tritiated water, due to their electrical repulsion by the negatively charged clay mineral surface (Van Loon *et al.* 2007; Tinnacher *et al.* 2016; Wigger and Van Loon 2017), but the true reason of anion exclusion could differ between Opalinus Clay and Boom Clay and the factor one half between diffusion accessible porosities of anions and HTO might be pure coincidence. As Opalinus Clay is very poor in smectite clay and also highly compacted, anion diffusion is mainly restricted by the narrow size of the pores between mineral grains (restriction to the inter-grain porosity). In the less compacted Boom Clay also containing smectite (14.2 wt% smectite + 15.3 wt % randomly interstratified illite/smectite, NEA, OECD 2022), anion exclusion could also be partly due to the restriction of anions to diffuse into the interlayers of smectite clay whose electrical double layers (EDL) overlap (restriction to the intra-grain porosity). On the other hand, the effective diffusion coefficients (D_e) of cations are higher than that of tritiated water (HTO) because of the enhanced surface diffusion occurring in the diffuse electrical double layer (diffuse EDL) of clay minerals enriched in cations to compensate the negative charges of clay minerals. These important advances in the understanding of enhanced cation surface diffusion were the result of a series of common works initiated in the context of the Mont Terri international collaboration and continued with several other partners of the European research framework in projects such as Funmig and CatClay (Altmann *et al.* 2015). These basic researches are still pursued today by the European Joint Programme EURAD on radioactive waste management, contributing to the dissemination of the knowledge acquired through the collaboration between HADES and Mont Terri URLs. With the notable exception of the smectite content (higher in Boom Clay), the nature and the contents of clay minerals in both formations (see Supplementary Materials, Table SM-3) are quite similar and responsible for the cation sorption and retardation in the Stern layer of the EDL and at the lateral edges of the clay platelets. The higher degree of compaction of Opalinus Clay, which was buried at much greater depth, and its much lower porosity, explain why its transport parameters (hydraulic conductivity and effective diffusion coefficients of radionuclides, see Supplementary Materials, Table SM-5) are more than one order of magnitude lower that these of Boom Clay at the Mol site.

Nitrate reactivity in clay formations

In several European countries, the disposal of nitrate-containing bituminized intermediate-level long-lived radioactive waste is still under investigation. Due to the presence of significant amounts of soluble nitrates in this waste form, a slow release of nitrate (and also a small amount of nitrite and organic degradation products) into the clay host rock is expected during geological disposal (Valcke *et al.* 2000*a*, 2009; Bleyen *et al.* 2018*a*, *b*). Nitrate is a potent oxidizing agent that can lead to positive redox conditions promoting the high oxidation states of redox-sensitive radionuclides. Such a nitrate plume in the clay formation could lead to biogeochemical perturbations of the clay and might therefore have a negative impact on the barrier function of the host rock towards radionuclide migration (Bleyen *et al.* 2018*a*). For example, the nitrate plume could affect the (initially reducing) redox conditions of the host rock surrounding the disposal facility due to nitrate reduction using clay components (e.g. organic matter, pyrite) as the electron donor. As the speciation, solubility, retention and transport properties of redox-sensitive radionuclides (Se, Tc, U, Np, Pu, etc.) is strongly affected by the redox conditions, a less reducing clay formation may enhance their migration in the host rock.

In the past 20 years, nitrate reactivity and diffusion have been investigated in several experiments in a reducing clay environment. As microbial activity cannot be ruled out in a repository for radioactive waste, both abiotic and microbial nitrate reduction processes have been studied, either separately or together, allowing for a correct understanding of the ongoing processes. At SCK CEN, several lab tests were performed under anoxic conditions, using clay cores and isolated redox-active Boom Clay components (organic matter, pyrite) obtained from the HADES URL. In addition, SCK CEN is conducting an *in situ* experiment at the Mont Terri rock laboratory, i.e. BN (or Bitumen–Nitrate–Clay interaction) experiment, which is performed in a packed-off and anoxic borehole, filled with artificial porewater, in equilibrium with the surrounding Opalinus Clay (shaly facies) (Bleyen *et al.* 2017, 2019). The design and interpretation of this *in situ* test benefited strongly from the knowledge obtained in the Porewater Chemistry (PC) experiment (see the 'Porewater chemistry experiments' section) and the previous successful diffusion experiments in the Opalinus Clay (see the 'Diffusion experiments' section).

Both experimental programmes have been running simultaneously, which allows for a fruitful exchange of knowledge, not only concerning the experimental design, but also for the interpretation of the results. Nevertheless, when comparing redox reactions in two clay formations, the differences in redox-active components in both clays need to be taken into account.

On the one hand, Fe(II) species such as pyrite (0.5–3.0 wt% in Boom Clay (Vandenberghe 1978; Decleer et al. 1983; Henrion et al. 1985; Baeyens et al. 1985a; Zeelmaekers et al. 2010, 2015; NEA Clay Club Catalogue, NEA, OECD 2022) and 0.4–2.2 wt% in the shaly facies of the Opalinus Clay (Pearson et al. 2003; NEA Clay Club Catalogue, NEA, OECD 2022) and organic matter (0.5–3.5 wt% in Boom Clay and 0.8–1.4 wt% in the shaly facies of the Opalinus Clay (Bossart 2017)) are deemed the most important redox-active species in both the Boom Clay and the Opalinus Clay. Due to differences in age and burial history, the natural organic matter in Boom Clay is considered more immature (and thus less recalcitrant) compared to the organic matter in Opalinus Clay which was exposed to a temperature of up to 85°C during several tens of million years when buried at great depth during the Cretaceous Period.

On the other hand, the chemical composition of the porewaters is very different (see also 'Porewater chemistry experiments' section) and their respective salinity may also significantly vary in space. For the lab tests performed at SCK CEN, Boom Clay porewater was sampled anoxically from the S-1D piezometer (formerly known as the EG/BS piezometer installed in the Boom Clay at the HADES URL; De Craen et al. 2004; Durce et al. 2015) underneath shaft 1 in the downward direction in the HADES URL. Overall the Boom Clay porewater is of the NaHCO$_3$-type (c. 15 mM). From a biochemical perspective, the main redox-active compounds are inorganic carbon (728–4425 mg l^{-1} HCO$_3^-$ in S-1D water) and DOM. In S-1D water, the latter is present at DOC concentrations of c. 80–160 mg C l^{-1} and has an average reducing capacity of 3.4 to 6.1 meq g C^{-1} (Bleyen et al. 2017). Low concentrations (<5 mg l^{-1} in S-1D water) of sulfate and dissolved Fe are detected as well (De Craen et al. 2004; Honty et al. 2022). In contrast, the Opalinus Clay porewater is of the NaCl type (c. 0.3 M, half-diluted seawater). The main redox-active compounds detected in the borehole solution of the BN experiment are sulfate (1059–1119 mg l^{-1}), inorganic carbon (34–62 mg l^{-1}) and DOC (c. 10 mg l^{-1}) (Bleyen et al. 2017).

Moreover, besides the lower DOC concentration in the Opalinus Clay porewater, the characteristics of the DOM are also different. In general, DOM in Boom Clay porewater is composed of more or less equal amounts of linear and aromatic structures. The DOM molecules are rather large in size, varying from a few 100 Da to larger than 100 kDa (Henrion et al. 1985; Deniau 2002; Blanchart 2011; Bruggeman and De Craen 2012; Durce et al. 2015). In water collected from the S-1D piezometer, formate and acetate concentrations remain below 0.5 mg l^{-1} (unpublished data). In contrast, the DOM in the Opalinus Clay porewater consists in part of lower molecular weight (and thus more biodegradable) molecules. About two-thirds of the DOC in porewater sampled from other boreholes in Opalinus Clay exhibit a molecular size lower than 500 Da and 30–40% of the DOC is made up of low-molecular weight organic acids, of which acetate (3–6 mg l^{-1} or 3–30% of DOC) is the most important, though formate (0.1–7.5 mg l^{-1} or 0.3–4% of DOC) and lactate (0.3 mg l^{-1} or 1% of DOC) are also present (Courdouan et al. 2007; Eichinger et al. 2011).

Taking the above-mentioned differences in geochemical composition into account, the knowledge obtained in each of the experimental programmes has proven to be useful to interpret the other one. Furthermore, both experimental programmes combined provide a good understanding of the ongoing processes and what can be expected when a nitrate plume enters a deep clay formation as explained in the next sections.

Long-term batch tests with nitrate and individual redox-active Boom Clay components (DOM or pyrite) or in Boom Clay slurries were performed to assess both the abiotic and microbially mediated reactivity of nitrate with Boom Clay components. These tests showed that nitrate does not (or not significantly) react abiotically (i.e. in sterile conditions) with either DOM or pyrite isolated from Boom Clay (Mariën et al. 2011; Bleyen et al. 2016a, b, 2018b; Hendrix et al. 2022) or in Boom Clay slurries, at least not within the experimental time scale (up to 3 years) (Mariën et al. 2011). When a microbial population is present, either already in the piezometer water (batch tests with DOM) or by inoculation (batch tests with pyrite), microbial nitrate reduction does occur, though it is characterized by very slow kinetics (e.g. 0.2–2 μM NO$_3^-$ day^{-1} in Boom Clay water with DOM as electron donor), indicating that Boom Clay DOM and pyrite are poorly bioavailable carbon sources and/or electron donors for nitrate-reducing microorganisms (Mariën et al. 2011; Bleyen et al. 2016a, b; 2021; Hendrix et al. 2022).

Percolation tests with nitrate at concentrations up to 1M in compact Boom Clay cores further confirmed that nitrate mostly diffuses through the clay as a non-reactive anion (Bleyen et al. 2018a). Only a limited nitrate reduction (to nitrite) was observed when percolating 0.1M NaNO$_3$. This reduction was

most likely to occur in the water tubings and the filters surrounding the clay cores, since it is generally accepted that microbial growth and microbial activity is restricted in undisturbed compact clay, due to the low porosity and the low amount of available water (Leupin *et al.* 2017). Increasing the nitrate concentration at the inlet to (presumably) toxic levels for nitrate-reducing microorganisms ($\geq$0.5M NaNO$_3$) prevented any further reduction of nitrate, again showing that abiotic reduction of nitrate by Boom Clay did not (or not significantly) occur in Boom Clay.

The results obtained *in situ* in the BN experiment at the Mont Terri Rock Laboratory are more or less in line with the results obtained in the lab batch tests with Boom Clay or its isolated components, including Boom Clay water alone no longer in contact with the buffering solid phase as presented in Figure 5. Injection of nitrate in the BN borehole that already contained a microbial population adapted to the Opalinus Clay environment resulted mainly in the diffusion of nitrate into the surrounding clay. Only a small part (about 11%) of the nitrate that was removed can be attributed to nitrate reactivity, and this at a rather slow rate (20–40 μM NO$_3^-$ day^{-1}) (Bleyen *et al.* 2017). Based on the results obtained from the batch tests with Boom Clay components, significant abiotic nitrate reactivity in the BN borehole can be considered unlikely, linking the observed reactivity to microbial activity. The microbial nitrate reduction is assumed to occur predominantly in the borehole, where sufficient space and water are available, and not in the surrounding

undisturbed and highly compacted Opalinus Clay Formation, similar to what was observed with the percolation tests performed with compact Boom Clay cores.

Note that the *in situ* nitrate reduction rate in the BN borehole in Opalinus Clay is more than 10 × higher than the one obtained in isolated Boom Clay porewater in laboratory batch tests as illustrated in Figure 5. This can be attributed to: (1) the *in situ* presence of other clay components around the test interval of the BN experiment, constantly replenishing nutrients (e.g. apatite as a source of phosphate) and energy sources, compared to the lack thereof in the lab batch tests with Boom Clay water alone isolated in a closed system and no longer in contact with the buffering clay minerals and solid organic matter; (2) the differences in the preservation of reducing conditions applied *in situ* and in lab experiments (also observed for other lab and *in situ* tests of the BN experiment; Bleyen *et al.* 2021); (3) differences in the characteristics of DOM in both clay formations, i.e. although the DOC concentration in Opalinus Clay porewater is lower than in Boom Clay porewater, its content in biodegradable species such as formate, acetate and lactate is higher (see above); (4) differences in the microbial communities thriving in the porewaters; and (5) a still undetected experimental artefact potentially affecting the BN experiment (in accordance with the perturbations introduced by the electrodes in the Porewater Chemistry (PC) experiment).

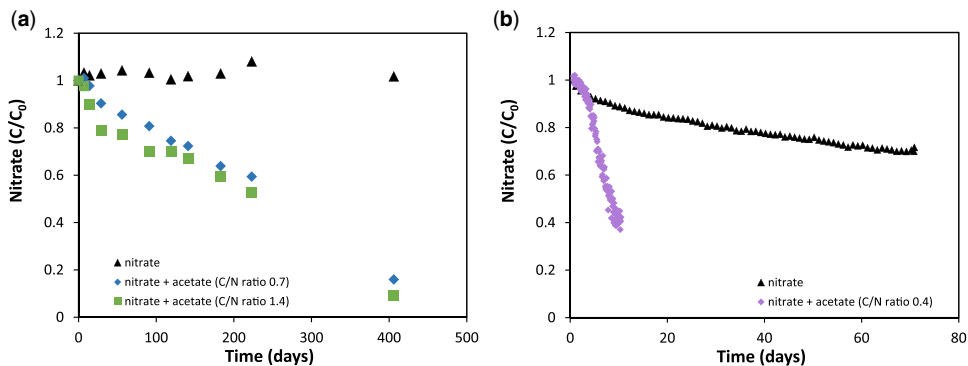In a geological repository, besides nitrate, also other water-soluble molecules stemming from the

Fig. 5. Relative concentration (C/C$_0$, where C$_0$ is the initial concentration) of nitrate in biotic laboratory batch tests with (**a**) pure Boom Clay water without contact with the solid clay phase (SCK CEN lab tests) and (**b**) Bitumen–Nitrate–Clay interaction (BN) experiment borehole water in contact with the Opalinus Clay Formation (*in situ*), with or without acetate addition (electron donor), as indicated in the legend. Note that the decrease in the nitrate concentration in the BN *in situ* experiment is due to a combination of diffusion from the borehole into the clay and nitrate reduction. Furthermore, in the BN *in situ* experiment, the constant supply of micronutrients from the solid clay surrounding the test interval, or the best preserved *in situ* conditions, probably considerably increases the reaction rate with respect to the lab tests with isolated Boom Clay water performed at SCK CEN. Source: data obtained from Bleyen *et al.* (2017, 2018*b*).

chemical and/or radiolytic degradation of bitumen are expected to leach from the waste packages into the surrounding clay formation. For nitrate-containing bituminized waste, acetate, formate and oxalate are the main organic degradation compounds presently identified (Valcke *et al.* 2000*a*, *b*, 2017). The impact of these easily metabolizable compounds on the microbially mediated nitrate reduction was therefore assessed as well, both at SCK CEN in lab tests with Boom Clay porewater from the S-1D piezometer and in the BN experiment in Opalinus Clay at the Mont Terri rock laboratory.

As can be observed in Figure 5a, addition of acetate to Boom Clay porewater containing nitrate strongly enhances the microbial nitrate reduction (by 200–700 times): in this system, acetate is clearly used as electron donor (Bleyen *et al.* 2018*b*). Similarly, as illustrated in Figure 5b, addition of acetate to the BN borehole already containing nitrate and a nitrate-reducing microbial community causes a clear increase (by up to *c.* 60 times) in the microbial nitrate reduction rates (Bleyen *et al.* 2017). Furthermore, in both experiments, addition of acetate resulted in a strong and rather quick shift in the microbial community, i.e. microbial species already having acetate-oxidizing enzymes are favoured and will thrive after acetate addition (Bleyen *et al.* 2017, 2018*b*). In Boom Clay porewater, acetate also seems to stimulate microbial degradation of DOM, shifting its average molecular size to slightly smaller sizes. This may have contributed, by a positive feedback due to smaller and more easily biodegradable organic molecules, to the higher relative increase in reaction rate observed in Boom Clay porewater (by 200–700 times) (Bleyen *et al.* 2018*b*) compared to the BN experiment (by *c.* 60 times) (Bleyen *et al.* 2017). However, when acetate is added as electron donor, the maximum reaction rates observed in the BN experiment (0.7–1.2 mM NO_3^- day^{-1}; Bleyen *et al.* 2017) and in Boom Clay porewater (0.2–0.7 mM NO_3^- day^{-1}; Bleyen *et al.* 2018*b*) are quite comparable. This suggests that the clay environment and the nature of DOM play only a limited role in the nitrate reactivity when microbes are fuelled with sufficient acetate.

In conclusion, although differences exist in the geochemistry of Boom Clay and Opalinus Clay, the experimental programmes addressing both clay formations are complementary and support each other. Based on the results obtained, nitrate reactivity seems to occur rather similarly in both clay formations. To verify and to complete these experiments, the reactivity of nitrate could also be directly assessed *in situ* in a piezometer installed in Boom Clay. The knowledge obtained so far in both experimental programmes represents added value for the design and the interpretation of the future results of such an experiment.

Unexpected findings and open questions

The open collaboration at Mont Terri was sometimes full of surprises and unexpected findings. As an example, one of the most serendipitous discovery in porewater chemistry is probably the discovery of an unexpectedly high partial pressure of N_2 gas (3.55 bar; log $pN_2 = 0.55$) dissolved in the clay porewater (Hydrogen Transfer (HT) experiment, Vinsot *et al.* 2014, 2017, 2018; Wersin *et al.* 2020, Nagra report NTB 18-01, pp. 88/108, table 4-11). If the porewater pressure is lowered below the pN_2 value, nitrogen would degas ('bubble point'). It is presently hypothesized that molecular nitrogen is formed and accumulated in the clay by the same mechanisms responsible for the generation and accumulation of N_2 in natural gas fields but the clay minerals could also play a specific role in the adsorption and transformation process of N-bearing natural organic matter under the effect of a thermal stress. This question of the deep N_2 gas source remains to be elucidated in the light of the well-studied nitrogen accumulation in natural gas fields (Littke *et al.* 1995; Gillaizeau *et al.* 1997; Behar *et al.* 2000) where sometimes N_2 concentration can even approach 100% of N_2 in high-risk exploration gas fields (Krooss *et al.* 1995). Stable isotope analysis ($\delta^{15}N$) could help identifying the N_2 primordial source. The effect of N_2 already dissolved in the pristine clay porewater on the fugacity (chemical activity of gases) of H_2 produced by anaerobic corrosion of steels and water radiolysis in a geological repository remains an open question that needs to be addressed in the frame of the gas studies. Indeed, this raises another, much more fundamental, question on the behaviour of multiple simple gases simultaneously dissolved in solution and their thermodynamic properties depending on their equation of state: if the clay porewater is at the same time saturated by dissolved N_2 and by dissolved H_2, could the presence of nitrogen (and the mutual physical interactions of the two dissolved gases co-existing in solution) contribute to significantly decrease the solubility of hydrogen? If the solubility in hydrogen gas is lower than anticipated in pure water for H_2, as usually considered as the only gas present in solution (simple binary system H_2–H_2O, the hypothesis implicitly assumed in the gas studies), this could lead to a decrease in the flux of the out-diffusing dissolved hydrogen in the clay porewater. The consequence for a radwaste repository in a deep clay formation is that the hydrogen gas breakthrough could be triggered at a pressure lower than expected with only H_2 alone in solution.

In a multicomponent simplified ternary system, such as H_2–N_2–H_2O, up to what point is it acceptable to consider that one uncharged simple gas species dissolved in porewater does not interact with the other one? Although a very fundamental question

in the thermodynamics of gas dissolution with direct implications in chemical engineering, this point still deserves to be explicitly addressed in the frame of the gas migration studies to rule out any unexpected problem overlooked up to now.

This is all the more important as the total gas pressure (from naturally existing dissolved N_2, CO_2 and CH_4 along with the generated H_2) is expected to increase with the smaller gas solubility at high temperature when the clay porewater will be heated around the high-level waste galleries (spent fuel and vitrified HLW). Another question to be addressed in the gas projects of the Eurad European Joint Programme (GAS and HITEC and their successors) is the following: could the thermal stress caused by the heat-emitting HLW also be able to generate extra N_2 gas in addition to CO_2 produced by the thermal degradation of kerogen (Deniau *et al.* 2005; Lorant *et al.* 2008)?

Overall cross-fertilization between HADES and Mont Terri

Even if the chemical and petro-physical properties of Boom Clay and Opalinus Clay are very contrasted in terms of mineralogy, porosity, microstructure, clay mineral swelling capacity, porewater content and composition, and geomechanical behaviour, they can be characterized by applying the same general principles and approaches with some adaptations when necessary.

The good collaboration and the cross-fertilization between the two underground laboratories and their research teams were essential because the pursued objectives are the same: to build robust and long-lasting repositories for radioactive waste in appropriate and stable geological formations and to demonstrate with sufficient confidence their long-term safety. It was therefore important to join efforts and to openly exchange scientific and technical knowledge to adequately characterize the respective potential clay host rocks under undisturbed natural conditions and also when the clay is submitted to thermo-hydro-mechanical solicitations and chemical perturbations. This allowed us to reinforce the scientific bases of the disposal system and to continuously question them when faced with unexpected behaviour or with inconsistencies in the different ways to approach the problems. The cross-fertilization between the two rock laboratories was fundamental for better understanding and more finely quantifying and reassessing critical phenomena and processes important for the safety and for the construction of deep geological repositories.

Cross-fertilization between HADES and Mont Terri gives the scientific community a large variety of experimental tools and modelling methods to characterize clay rocks not only in the frame of deep geological disposal of radioactive waste but also for other uses of the underground, such as the correct management of natural resources becoming increasingly rare (water, oil and gas), CO_2 storage (to tackle climate changes) and applications in the field of geothermal energy. In the context of the ecological turnaround, the production and distribution of heat is an important element to consider in the strategies to reduce CO_2 emissions. As the available heat is out of phase with the demand (summer, winter), seasonal heat storage possibilities would allow a much more rational use of the available resource. One solution of storage envisaged is injection and storage in the subsurface. The injection must be done at a sufficient depth not to threaten the underground drinking water resource. Very often at the targeted depths, the available aquifers are in hard rock, fractured and/or karstified. To implement this strategy, it is necessary to better understand the transport and exchange of heat in fractured media. Thanks to the experiences gained in the framework of deep geological disposal of radioactive waste, it was easy to extend the research programme with a new experiment called 'Aquifer thermal energy storage in fractures limestones' started in 2022 at Mont Terri.

Future collaboration between HADES and Mont Terri

SCK CEN and FANC will be participating in several experiments at Mont Terri, which have been started recently or will be performed in the near future.

Firstly, FANC and SCK CEN joined the GT experiment (Evaluation of Gas Transport models), which started at Mont Terri in 2021. The main goals are to define a conceptual gas transport model, to assess the behaviour of Opalinus Clay to gas pressure, to understand micro- and macro-fracture creation (capillary entry pressure v. minimum principal stress) and finally to compare laboratory and field experiments.

Secondly, a new diffusion experiment (DR-E) was installed at Mont Terri in January 2023, and the injection of tracers will be performed after the borehole is sufficiently equilibrated with the surrounding clay. The main goal of this study is to investigate tracer diffusion within the steeply dipping Main Fault zone within the Opalinus Clay to provide/confirm effective transport parameters of radionuclides in tectonically affected zones and discontinuities for safety assessment calculations. This study is based on previous successful long-term tracer diffusion experiments (FM-C, DI, DI-A, DI-B, DR, DR-A, DR-B and so on) in the Opalinus Clay where diffusion within undisturbed and bedded zones was monitored and analysed. There, the

diffusion processes of weakly sorbing and non-sorbing tracers are well documented and the results from laboratory and field experiments agree. The novelty of the new DR-E diffusion experiment is to investigate tracer migration within the Main Fault zone by adapting the downhole equipment of the borehole to a highly fractured and incompetent indurated claystone. Because of the mechanical weakness of the faulted zone, the final overcoring will also be challenging. FANC with its experience in radionuclide transport in Opalinus Clay is partner of this new experiment proposal.

Finally, collaboration between SCK CEN, FANC and Mont Terri will continue in the ongoing experiments in the fields of geochemistry, diffusion of radionuclides and THM experiments.

Conclusions

The collaboration between the HADES URL and the Mont Terri rock laboratory led to significant technical improvements in measuring instruments required for the experimental determination of parameters (porewater pressure, pH, E_h) directly performed *in situ* on the site. This contributed to advance the understanding of the evolution of geological disposal systems in clay formation. New measuring instruments specifically designed and adapted for hard clay formations were developed, such as a piezometer for measuring the porewater pressure, a challenging task in a highly consolidated low-permeability hard claystone. Further, scientific and technical exchanges between the two underground laboratories in the field of geochemistry and microbiology helped to identify the root cause of an unexpected microbial perturbation fuelled by the organic carbon released by the pressure-resisting electrodes and affecting the on-line pH and E_h measurements. It allowed the development of new measuring systems to investigate new emerging topics such as the study of the geochemical and microbiological perturbations caused to the clay by a nitrate plume released by bituminized intermediate-level waste. In the field of geomechanics, the main scientific finding was the similar behaviour of highly and poorly consolidated clays formations in response to the thermo-hydro-mechanical perturbations. For instance, despite some significant differences in their geomechanical properties, both types of clay formations respond in a quite similar way to excavation as revealed by the porewater pressure variations during mine-by tests while the fractures network developed in the excavation disturbed zone exhibits the same characteristic herringbone patterns. Without this co-operation, the work would have been much more difficult and time consuming. From a scientific perspective, the collaboration has led to significant advances in the fields of geochemistry, microbiology, diffusion of radionuclides and the understanding of thermo-hydro-mechanical processes in clay formations.

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Data availability Data sharing is not applicable to this article as no datasets were generated or analysed during the current study.

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