

Applying Squeezing Technique to Clayrocks: Lessons Learned from Experiments at Mont Terri Rock Laboratory

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Catálogo general de publicaciones oficiales
<http://www.060.es>

Depósito Legal: M -26385-2011

ISSN: 1135 - 9420

NIPO: 721-13-054-0

Editorial CIEMAT

CLASIFICACIÓN DOE Y DESCRIPTORES

S58

PHYSICAL PROPERTIES; CHEMICAL PROPERTIES; CLAYS; MINERALS;
GEOCHEMICAL SURVEYS; SPAIN

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88 pp. 173 ref. 39 figs.

Abstract:

Knowledge of the pore water chemistry in clayrock formations plays an important role in determining radionuclide migration in the context of nuclear waste disposal. Among the different in situ and ex-situ techniques for pore water sampling in clay sediments and soils, squeezing technique dates back 115 years. Although different studies have been performed about the reliability and representativeness of squeezed pore waters, more of them were achieved on high-porosity, high water content and unconsolidated clay sediments. A very few of them tackled the analysis of squeezed pore water from low-porosity, low water content and highly consolidated clayrocks.

In this work, a specially designed and fabricated one-dimensional compression cell two directional fluid flow was used to extract and analyse the pore water composition of Opalinus Clay core samples from Mont Terri (Switzerland). The reproducibility of the technique is good and no ionic ultrafiltration, chemical fractionation or anion exclusion was found in the range of pressures analysed: 70-200 MPa. Pore waters extracted in this range of pressures do not decrease in concentration, which would indicate a dilution of water by mixing of the free pore water and the outer layers of double layer water (Donnan water). A threshold (safety) squeezing pressure of 175 MPa was established for avoiding membrane effects (ion filtering, anion exclusion, etc.) from clay particles induced by increasing pressures. Besides, the pore waters extracted at these pressures are representative of the Opalinus Clay formation from a direct comparison against in situ collected borehole waters.

Aplicando la Técnica de Consolidación a Alta Presión en Rocas Arcillosas: Lecciones Aprendidas en Ensayos del Laboratorio de Investigación de Mont Terri

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Resumen:

Dentro del contexto del almacenamiento de residuos radiactivos, el conocimiento de la química del agua intersticial en formaciones arcillosas juega un importante papel en la evolución de la migración de radionucleidos. Entre las diferentes técnicas *in situ* y *ex-situ* de extracción del agua intersticial en sedimentos arcillosos y suelos, la técnica de *squeezing* se remonta a hace 115 años. Aunque se han realizado muchos estudios sobre la fiabilidad y representatividad del agua extraída por consolidación a alta presión, muchos de ellos se han realizado en sedimentos no consolidados, de alta porosidad y elevado contenido de humedad. Muy pocos han tratado sobre rocas arcillosas altamente consolidadas, de muy baja porosidad y con bajos contenidos de humedad.

En este trabajo, se utilizó una celda especialmente diseñada para extraer y analizar el agua intersticial de la formación Opalinus Clay de Mont Terri (Switzerland), con contenidos de agua entre el 6.2 y 7.8%. La reproducibilidad de la técnica es buena y no se han encontrado procesos de ultrafiltración iónica, fraccionamiento químico o exclusión aniónica en el rango de presiones analizadas: 70-200 MPa. Se ha establecido una presión umbral de 175 MPa para evitar los posibles efectos de membrana de las partículas de arcilla inducidos por el incremento de la presión. Además, las aguas extraídas a estas presiones son representativas del agua de la formación por comparación directa con aguas obtenidas *in situ* por percolación mediante sondeos obturados.

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ABSTRACT

Knowledge of the pore water chemistry in clayrock formations plays an important role in determining radionuclide migration in the context of nuclear waste disposal. Among the different *in situ* and *ex-situ* techniques for pore water sampling in clay sediments and soils, squeezing technique dates back 115 years. Although different studies have been performed about the reliability and representativeness of squeezed pore waters, more of them were achieved on high-porosity, high water content and unconsolidated clay sediments. A very few of them tackled the analysis of squeezed pore water from low-porosity, low water content and highly consolidated clayrocks.

In this work, a specially designed and fabricated one-dimensional compression cell two directional fluid flow was used to extract and analyse the pore water composition of Opalinus Clay core samples from Mont Terri (Switzerland) having water contents between 6.2 and 7.8%. A study of the influence of the squeezing pressure on the chemistry of the pore water was performed until 200 MPa. To validate and demonstrate the veracity of the squeezing technique for obtaining the reliable pore water, different tests were performed at different pressures and squeezed waters were compared with those obtained by other methods, such as *in situ* collected borehole waters. The reproducibility of the squeezing method was also checked, as well as different artefacts which could influence of the reliability of the pore water data.

As result, reproducibility of the technique is good and no ionic ultrafiltration, chemical fractionation or anion exclusion was found in the range of pressures analysed: 70-200 MPa. Pore waters extracted in this range of pressures do not decrease in concentration, which would indicate a dilution of water by mixing of the free pore water and the outer layers of double layer water (Donnan water). A threshold (safety) squeezing pressure of 175 MPa was established for avoiding membrane effects (ion filtering, anion exclusion, etc.) from clay particles induced by increasing pressures. Besides, the pore waters extracted at these pressures are representative of the Opalinus Clay formation from a direct comparison against *in situ* collected borehole waters. Artefacts during extraction such as temperature effect, oxidation, degassing can be avoided or minimized by taking special precautions during sample preparation and handling and pore water extraction. Finally, we show that it is possible to obtain insightful information from squeezing data combined to aqueous leaching data for characterising the pore water composition and solutes distribution in the different porosity types of the rock.

Keywords: Squeezing, Pore water, Consolidated clayrocks, Opalinus Clay, Anion exclusion, Membrane effect, accessible porosity

1. INTRODUCTION

Argillaceous Rocks of low permeability have been selected in several countries such as Belgium, Switzerland and France (Ondraf-Niras, 2001; Nagra, 2002; Andra, 2005) as potential geological host rocks for the disposal of high level radioactive wastes (HLRW). The host-rock represents the most important barrier to the migration of radionuclides to the surface environment, and clay minerals have favourable properties, such a large sorption capacity (ion exchange and surface complexation) and low permeability, which reduce water movement. Pore waters of clayrocks are generally reducing with neutral pH values, ensuring that the solubilities of a large number of radioelements will be very low. Besides, the swelling capacity of some clay particles will cause sealing of potential fractures, and thus significant retardation in the transport of most radionuclides (Horseman and Volckaert, 1996).

In order to determine the suitability of these clayrocks for waste disposal, evaluations of the hydrogeochemistry and transport mechanisms from such geological formations to the biosphere must be undertaken. One of the crucial questions about radionuclide diffusion and retention is to know the chemistry, chemical reactions and sorption processes that will occur in the rock and their effects on radionuclide mobility. The migration of radionuclides through the geosphere will occur predominantly in the aqueous phase, and hence the pore water chemistry plays an important role in determining radionuclide migration characteristics in clay-rock formations, especially as regards actinides and other redox sensitivity elements (Bradbury and Baeyens, 1998; Altmann, 2008; Mazurek et al., 2009).

Furthermore, a knowledge of the chemical composition of the clayrock pore waters is essential for the design of safety scenarios because: 1) it provides necessary input data for characterising the geological barrier ability to: a) retain radionuclides chemically (retention (K_d) and solubility), and b) to limit the transport of radionuclides (speciation and accessible porosity); and 2) it establishes the base line chemistry of the undisturbed system to estimate the evolution of structural components (waste matrix dissolution, canister corrosion, sorption of mineral surfaces dissolution of packages and containers, engineered barriers degradation: bentonite, concrete, etc.), contributing in the engineering design and the chemical modelling of radionuclides in the near and far field environments.

Therefore, collection of representative pore water solutions in clayrocks is one of the main objects of any hydrogeochemical research program in argillaceous formations. A large effort has been undertaken to characterise the pore water chemistry in selected clayrock formations in Europe: Boom Clay (Belgium), Opalinus Clay (Switzerland) and Callovo-Oxfordian (France) formations in order to understand the underlying geochemical processes and to establish a reliable model for the main water-rock interactions which control the physico-chemical parameters and the chemistry of the major elements in the clay-water-solute system.

However, recovering the pore water solution representative of *in situ* conditions from low permeable and low water content systems is very difficult and sometimes impossible due to their properties: low permeability, high retention capacity, very high ratios of mineral surface area to pore solution volume, and the strong interactions between the pore water and clay mineral surfaces, which implies different types of water as a function of the porosity size they are associated with (macro-, meso- and micro-porosities).

One of the most important problems in the study of the pore water chemistry in clayrocks is the validity of the sampling procedures. The clayrock-pore water system is a complex combination of an ion exchange matrix and other solid material that may be in equilibrium with the interstitial fluids. Recovery of the interstitial water under different *in situ* conditions of temperature, pressure and oxidation state may lead to results distinct from the real situation. Several review studies about the pore water chemistry of clayrocks and extraction techniques have been performed over time (Sacchi et al., 200; 2001; Bath et al., 2001; Pearson et al., 2003). In these reviews the difficulty of sampling undisturbed pore water from clayrocks is emphasized because of their low permeability and the oxidation of organic matter and pyrite by atmospheric oxygen during sampling analysis.

Research efforts over the last 15 years have been focused on developing techniques for determining pore water composition of clayrocks in the context of waste disposal including both direct methods (from borehole core samples or dedicated experiments carried out in underground research laboratories, URL), and indirect methods (from modelling):

1. *In situ* pore water sampling (water and gas) from sealed boreholes drilled from the rock laboratory, which offers direct measurements of seepage water chemistry (Pearson et al., 2003; De Craen et al., 2004a; Vinsot et al., 2008a).
2. Laboratory pore water sampling from unaltered core samples by the Squeezing technique at high pressures (Entwisle and Reeder, 1993, 1989; Fernández et al., 2003; De Craen et al., 2004b) or advective displacement experiments (Mäder et al., 2004).
3. Characterization of water chemistry by geochemical modelling based on: a) measured laboratory properties of the rock, such as mineralogy, physical properties (water content, dry density, porosity), physico-chemical properties (cation exchange, cation exchange population, surfaces areas, cation exchange selectivity coefficients, surface complexation properties, diffusion coefficients, etc.); b) fixed concentration of non-reactives solutes (anion inventories); c) constrains regarding to mineral, cation exchange and redox equilibria; d) understanding of the water-rock reactions and transport processes implicated in the clayey system; and e) a good selection of the thermodynamic database (Baeyens and Bradbury, 1994; Bradbury and Baeyens, 1998; Beaucaire et al., 2000; Arcos et al., 2001; Pearson et al., 2003; de Craen et al., 2004b; Gaucher et al., 2009; Appelo et al., 2008; Pearson et al., 2011).

From these techniques, squeezing has been widely used for analyzing the pore water chemistry in this context and other scientific fields: soils, marine geochemistry and diagenesis of sediments.

1.1. Why is necessary to obtain the pore water by the squeezing technique in the context of radioactive waste disposal?

There are four main reasons of why is necessary the *ex-situ* pore water collection by the squeezing technique in the context of radioactive waste disposal:

- 1) Measuring the *in situ* composition of clayrocks pore water from packered boreholes drilled in a Rock Laboratory is expensive, compared to laboratory tests, and the results are often modified by experimental artifacts: oxidation, outgassing, microbial growth, and mechanical stress (Wersin et al., 2011; Vinsot et al., 2008);
- 2) Ex-situ water collection methods are often necessary when *in situ* water collection is not viable, or requires long sampling times, when a brief sampling time is critical for chemical characterization;
- 4) The associated solid phases cannot be recovered. Squeezed pore water and rock properties can be used to obtain the anion-accessible porosity parameter, necessary for inferring the pore water composition indirectly by geochemical modeling;
- 5) Squeezing technique can be used to obtain the osmotic suction of clayey materials by measuring the electrical conductivity of the pore water because total concentration of dissolved salts is related to the osmotic suction
- 6) Modeling work aims at understanding the processes for pore water composition controls and helps to extrapolate these results to other locations where water samples are not available. However, confidence in modeling work results ultimately rely on a good agreement between predictive models and *in situ* or squeezing measurements (Vinsot et al. 2008b, Gaucher et al., 2009, Pearson et al., 2011).

Therefore, squeezing technique can then be a good alternative method to measure the pore water composition.

In this work, a study of the pore water chemistry of the Opalinus Clay formation at Mont Terri is performed by using the squeezing technique. Besides, the influence of the pressure up to 200 MPa is examined evaluating all the possible causes and suggesting a threshold squeezing pressure for this clayey formation. The squeezing study of the Opalinus Clay core samples over more than 12 years in the context of the “Geochemical Modelling Task” from the Mont Terri Project allowed to check the

representativity and the reproducibility of the squeezing technique for the analysis of the ion and isotope data in the pore waters. A number of factors that may influence on the reliability of pore water chemical composition extracted by squeezing, such as: a) rock sampling and decompressional effect, 2) handling, preservation, storage period and conditions prior to extraction of interstitial waters, 3) temperature elevation during interstitial waters extraction during core drilling and through squeezing 4) pressure exerted during squeezing, 5) degassing, and 6) oxygen contamination during drilling, storage and squeezing, is discussed. Besides, a complete summary of the squeezing studies performed over time is outlined. Finally, an anion accessible porosity for chloride is determined in this formation.

2. State of the art of the Squeezing Technique

2.1. What is squeezing?.

Squeezing is analogous to the natural process of consolidation, caused by the deposition of material during geological time, but at a greatly accelerated rate. The squeezing process involves the expulsion of interstitial fluid from the saturated argillaceous material being compressed (Entwisle and Reeder, 1993). Liquids may be removed from a saturated porous medium if the pore space can be sufficiently reduced by compaction. When a stress or load applied to a soil or sediment is suddenly changed, this change is absorbed jointly by the interstitial fluid and the mineral skeleton as a consequence of the discontinuous nature of the sediment (composed of solid particles and spaces or voids filled with water in saturated rocks). The change in pore pressure will cause water to move through the soil, hence the properties of the soil will change with time (Terzaghi, 1920).

When a squeezing stress is applied to water saturated clayrock, its volume decreases mainly by the escape of pore water from the voids following Darcy's Law, because in most circumstances the compression of the solid phase and water phase is negligible. The volume change is related to the applied pressure and the difference between the applied pressure and the interstitial pressure (Yong and Warkentin, 1975). As the stress increases, the pore water pressure increases and the excess of pore pressure dissipates by means of the expulsion of the water from the material (Figure 1).

The dissipation of the pore water pressure by the gradual expulsion of water, due to the stress applied, is called *primary consolidation*. The water extracted during squeezing is mainly due to primary consolidation and the time for this to occur is the *hydrodynamic shift*. The rate of consolidation produced up to a given instant depends not only on the applied stress, but also on the intensity of the transmitted stresses in the particle contacts, i.e. on the difference between the applied stress and the pore pressure. During any time interval only a limited water flux can occur.

The time required for the consolidation process should be related to two factors (Lambe and Whitman, 1994): 1) directly proportional to the volume of water which must be squeezed out of the soil, which is in turn, related to the product of the stress change, the compressibility of the mineral skeleton and the volume of the soil; and 2) inversely proportional to how fast the water can flow through the soil. The velocity of flow is related to the product of the permeability and the hydraulic gradient, and the gradient is proportional to the fluid pressure lost within the soil divided by the distance through which the pore fluid must flow. These considerations can be expressed by the relationship:

$$t = \frac{(\Delta\sigma)(m)(H)}{(k)(\Delta\sigma/H)} \sim \frac{mH^2}{k} \quad \text{Eq. 1}$$

where,

t = the required time to complete some percentage of the consolidation process (s), $\Delta\sigma$ = the change in the applied stress (kg/cm^2), m = the compressibility of the mineral skeleton (cm^2/kg), H = the thickness of the soil mass (per drainage surface) (cm), and k = the permeability of the soil (cm/s).

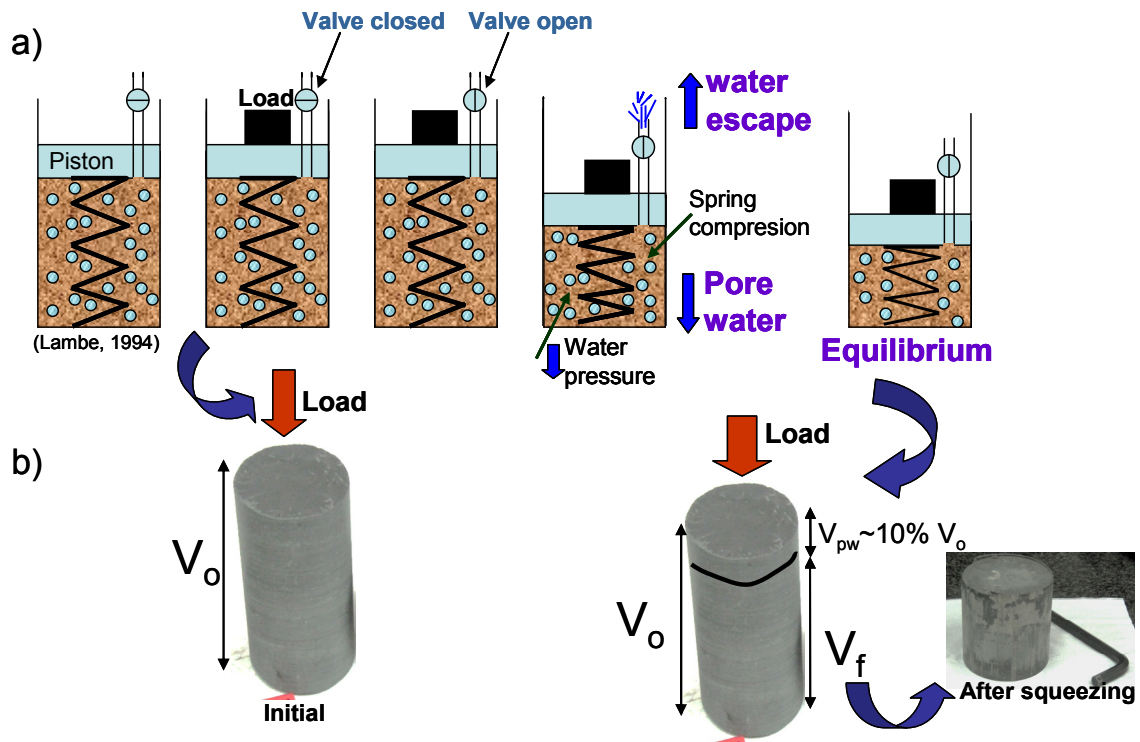


Figure 1. a) Hydromechanical analogy for load changes during squeezing and consolidation (Lambe and Whitman, 1969): The resistance of the internal phase compression is represented by a spring and the rate at which the pore water flows is dependent on the size of the valve aperture. First the valve is closed and in equilibrium. When a load is applied, the piston load is apportioned by the water and the spring in relation to the stiffness of each. All the applied load is resisted by an increase in the fluid pressure. If the valve is opened, the excess of pore pressure will dissipate by water escaping through the valve. The piston drops and the volume chamber decreases until there is a new equilibrium when the load is carried by the spring and the water pressure has returned to the original hydrostatic condition; **b) Illustration of the reduction of volume, V_o to V_f , of a saturated core sample from Opalinus Clay (BHT-1 m. 12.42) after a squeezing test. The volume of expelled pore water is represented by V_{pw} .**

This relationship implies that the consolidation time: 1) increases with increasing compressibility; 2) decreases with increasing permeability, 3) increases rapidly with increasing size (thickness) of the soil mass, and 4) it is independent of the magnitude of the stress variation.

The rate of water extraction when a saturated clayrock is compressed artificially in a squeezing test is partly controlled by the stiffness and the permeability of the material tested. The main constraint on whether water can be extracted is the stiffness of the sample to be squeezed. The water extracted under each stress increment, or in total, can be related to the change in voids ratio, e (the ratio of the volume of the voids to the volume of the grains) or to the change in the porosity (Rieke and Chilingarian, 1974). In a saturated material, the potential amount of extracted water is the excess of water coming from the consolidation of the material under stress, i.e. the amount of water enclosed in the voids between the final and initial volumes of the sample (Figure 1b). The increasing stress, which is commonly added incrementally in a squeezing test, produces a reduction of pore size thus reducing the permeability, the rate of consolidation and the rate of water extraction.

As conclusion, in squeezing experiments the expulsion rate of the pore fluid is related to the permeability, the length and the pore size of the rock sample. The volume of water extracted depends basically on the initial water content of the sample, the rock properties (e.g. dry density, the relative contents of easily-squeezed clays and of stiffer materials like quartz and calcite), the squeezing pressure applied, the squeezing time and the size of the squeezing apparatus (volume and diameter).

2.1.1. *What is a squeezer?*

The approaches developed may be more sophisticated but the principle is the same: forcing pore fluid through a membrane by applying pressure to a wet sediment. In its many forms, the “squeezer” is essentially a cylinder with a supported membrane at its base(s) into which the sediment samples is placed. A piston (or diaphragm) is then inserted into the cylinder and force is applied to the piston, forcing the expulsion of the pore water from the base of the cylinder.

The main approach used by investigators has been one of innovation and modification of the high-pressure apparatus, namely consolidometer. In the consolidometer, a sample undergoes deformation (one-dimensional consolidation or compaction) in response to the unidirectional applied pressure, a definitive volume change occurs in the sample with increasing axial load on the sample as well as mass changes because fluid is expelled from the sample owing to the volumetric change within the sediment sample.

There are four basic requirements that should be met by the equipment used in investigating the chemical and mechanical properties of sediments or clays under high pressures (Rieke and Chilingarian, 1974): 1) application of a uniform stress on the contained sample, 2) measurement of the resulting sample deformation, 3) channeling and collection of the expelled fluid, and 4) utilization of a sample of sufficient size so that representative information can be obtained.

Although equipment design criteria can vary depending on the investigation (Table 1, Table 2, Annex A), there are certain main points common to all: 1) the squeezer must be reliable, 2) removal of water must be achieved in such way that the composition is not changed, 3) the sediment sample must be larger enough so that a sufficient amount of fluid can be obtained, 4) evaporation must not occur, and 5) the sample must not squeeze-by (Rieke and Chilingarian, 1974).

2.1.2. *Historical developments about the study of interstitial fluids*

Compaction equipment used for the characterization of geological materials are classified on the basis of how the pressure is applied (Table 1). The pressure-transmitting media may be: a) mechanical, by means of a ram or a lever (wheel); or b) fluid, being this either a liquid (such as oil, mercury or hydraulic fluid), or a gas (such as nitrogen, argon or helium). Different compaction equipments have been developed on time with different purposes (Rieke and Chilingarian, 1974), such as to study the compressibility and thermodynamics properties of liquids (e.g. Canton, 1762; Barus, 1892), deformation of rocks (e.g. Adams and Nicholson, 1901); bulk compressibilities of minerals and rocks (e.g. Adams and Williamson, 1923), rock deformation under high confining pressure (e.g. Griggs, 1936), mixture of complex hydrocarbon at elevated temperatures and pressures (e.g. Sage and Lacey, 1948), volumetric behaviour of hydrocarbon systems (e.g. Standing, 1952), synthesis of diamonds (e.g. Hall, 1961), and plastic deformation and recrystallization of quartz (Carter et al., 1964). In studying the chemistry of the interstitial fluids of sediments and clayrocks, the problem of extracting such fluid was solved by using these types of compaction equipments (especially consolidometers) or a modification of these. A detailed review of pore fluids extraction techniques including pressure filtration and squeezing can be found in Kriukov and Manheim (1982), Adams (1994), Reeder et al. (1998) and Sacchi et al. (2000, 2001).

Nowadays most of the techniques applied to consolidated clayrocks for analysing the composition of fluids components came from studies in Ocean sediments and Soil Chemist performed since early this century. The first reported study using the squeezing technique to sediments is from Murray and Irvine (1895). In 1872, the H.M.S. Challenger expedition marked the beginning of many new scientific techniques in oceanography. Sir John Murray, the pioneer British oceanographer, in conjunction with R. Irvine, applied the squeezing technique to obtain fluids from a shallow Scottish coast sediment (blue terrigenous muds from the seafloor) in a canvas bag and caught and analysed the drippings.

Table 1. Classification and application of compaction apparatuses used in the investigation of geochemical and geodynamic problems

Pressure application		Apparatus Type and approximate maximum pressure	Application	References
Mechanical pressure system	Linear Piston (L≤D)*	Consolidometer: 13.8-324 MPa	<ul style="list-style-type: none"> • Compression of clays and sediments • Permeability of clay membranes to salt solutions 	Terzaghi (1925), Casagrande (1932), MacKelvey and Milne (1962), Von Engelhardt and Gaida (1963)
		Filter press (Whole-core section)/Low pressure squeezer (Manual or Hand screw plunger): 2 MPa	Chemistry of solutions squeezed out of Recent sediments and marine sediments	Shepard and Moore (1955), Siever (1962)
	Linear Piston (L>D)	Single-Volumometer piston: 1400 MPa	P-V-T-S(**) relationships of water	Kennedy (1950)
		Single-state piston (one directional fluid flow): 138 MPa	<ul style="list-style-type: none"> • Chemistry of solutions squeezed out of marine sediments • Chemistry of solutions squeezed out of Clayey formations and bituminous shales (with and without temperature) 	Buneeva et al. (1947), Kriukov and Komarova (1954), Chilingar et al. (1963a), Kryukov (1961, 1964), Manheim (1966), Kazintsev (1968)
		Dual or duplex piston (two directional fluid flow): 68-3500 MPa	Clay compaction and fluid extraction	Kryukov (1961), Chilingar and Knight (1960), Rieke et al. (1969), Van der Knaap and Van der Vlis (1967)
Multiple Piston (L≥D)	Anvils: 1034 MPa	<ul style="list-style-type: none"> • Material Science: effects of P and T • Mineral and diamond synthesis 	Bridgman (1918, 1937), Hall (1958), Giardini et al.(1960), Bundy (1962)	
Fluid pressure system	Hydraulic fluid	Triaxial, hydrostatic: 275 MPa	<ul style="list-style-type: none"> • Petroleum engineering research. • Compressibility of porous materials. • Strain and temperature on the behaviour of rocks. • Interstitial water from coarse-grained sediments. 	Hall (1953), Fatt (1953), Scholl (1963), Heuer et al. (1965), Sawabini et al. (1971)
	Kerosene	Pressure cell	Volume changes in solids, including quartz and calcite	Adams et al. (1919)
	Mercury	P-V-T cell: 103 MPa	P-V-T relationships of hydrocarbons	Sage et al. (1934), Standing (1952)
	Gas	Filter press (core section)/Low pressure squeezer: 6.9 MPa	Chemistry of solutions squeezed out of marine sediments and hydrated montmorillonite and illite clays	Richards (1941), Luczynski (1961), Siever (1962), Hartman (1965), Gann (1965), Reeburgh (1967), Presley et al. (1967), de Lange (1992), de Lange et al. (1992)

(*) L = length and D = Diameter of the piston. (**) Pressure-Volume-Temperature-Salinity

Table 2. Comparison of mechanical squeezing tests performed over time

Type of squeezers	Squeezer components and characteristics	Pressure	Type of samples	Water content/ Porosity	Amount of sample	Extracted volume	Squeezing Time	References
Low pressure Filter press (Whole-core section) /	Squeezer cells made of SS or non-metallic components (Delrin, nylon, dental-dam rubber, Plexiglas, Teflon), Thermoregulated	0.3-7 MPa	Marine and lacustrine sediments	40-100 wt.% / 50-90%	100-200	20-100 g	10 min.-4 hours	Kalil & Goldhaber (1973); Bender et al. (1987); Jahnke (1988); Patterson et al. (1978); Sasseville et al. (1974)
High Pressure Single-state piston (one directional fluid flow, core section)	303 Stainless steel (Ø=28.6 mm, h= 76.2 mm) (Ø=42.7 mm, h= 76.9 mm)	4-82 MPa	Recent to Paleocene marine sediments (DODP) and Pliocene-Recent Clayey Sediments	20-60 wt.%	2-15 g	1-15 g	3 min.	Manheim (1966) Manheim and Bischof (1969) Manheim et al. (1994), Ridout (1981)
	303 Stainless steel (Ø=28.6 mm, h= 76.2 mm)	4.8-52 MPa (selected: 6.8 MPa)	Brearpaw Shale and Moden Shale: Upper Cretaceous Marine plastic deposits (Canada)	18-54 wt.%	--	5 g	4 hours-12 hours	Morgenstern & Balasubramonian (1980), Iyer (1990)
	Alloy Stainless steel Thermoregulated (Ø=75 mm, h= 100 mm)	10-110 MPa	Cretaceous-Jurassic mudrocks (Oxford Clay at Hardwell Research Site)	16-40 wt.% / (~30%)	400-650 g	18-52 g (14-64 of total water content)	2-9 days	Brightmann et al (1985) Ross et al. (1989)
	316 Stainless steel Thermoregulated, Anoxic condions (Ø=75 mm, h= 100 mm)	10-70 MPa	Mesozoic and Tertiary mudrocks (London Clay at Bradwell Site)	20-53 wt.% / (~48%)	485-900 g	16-99 g (15-63% of the total water content)	1-3 days	Bath et al. (1989) Entwistle & Reeder (1993)
	Titanium (Ø=20 mm, h= 35 mm)	100-120 MPa	Resaturated MX-80 bentonite	13-22 wt.%	--	0.5-3 g	7-15 days	Muurinen & Lehtikoinen (1999) Murinen & Carlsson (2007)
Oedometer press + Hydraulic press	316 Stainless steel (Ø=50 mm, h= 45 mm)	75-150 MPa	Plio-Pleistocene marginal and fluvio-lacustrine clay formations	16-34 wt.%	--	10-23 g (52-80% of the total water content)	9-20 days	Fontanive et al. (1995)
Triaxial-oedometer (core section)	4140-alloy steel (Ø=61 mm, h= 110 mm)	Confining stress: 69 MPa Axial stress: 193 MPa	Unsaturated tuffs (Yucca Mountain, USA)	8-32 wt.%/22-58%	400-600 g	3-55 g	6-8 hours	Yang et al. (1988, 1995)
High Pressure Dual piston (two directional fluid flow, core section)	C250 Maraging Steel (Ø=61 mm, h= 110 mm)	34-827 MPa	Unsaturated nonwelded and densely welded tuffs (Yucca Mountain, USA)	5.3-31 wt.% / 16-51%	400-600 g	6-24 g (16 to 60 % for nonwelded tuff cores, 2 to 28 % for densely welded tuff cores)	4 hours-1 day	Peters et al. (1992) Mower et al. (1994) Higgings et al (1996)
	Al with polyamide liners and Teflon filter holders (Ø~50 mm, h~ 76.2 mm)	25-108 MPa	Fine fraction of soils	22-35 wt.%	150-200 g	8-36 g (20-55% of the total water content)	1 hour	Böttcher et al. (1997)
	329 Stainless steel (Ø=70 mm, h= 250 mm)	10-64 MPa	Bentonite FEBEX from Cortijo de Archidona quarry (Spain)	14-53 wt.% / 40-56%	400-1000 g	33-121 g (10-50% of the total water content)	4-37 days	Fernández (2004) Enresa (2000, 2006)
	329 Stainless steel (Ø=70 mm, h= 500 mm)	70-200 MPa	Opalinus clay (Switzerland)	7-8 wt.% / 17%	500-700 g	1-5 g	8-15 days	Fernández et al. (2003)
	316L Stainless steel (Ø=80 mm, h= 100 mm)	30 MPa	Boom Clay (Belgium)	22 wt.% / 36%	700 g	40-50 g (30-35% of the total water content)	7 days	De Craen et al. (2004)
	329 Stainless steel (Ø=70 mm, h= 500 mm)	70-200 MPa	Callovo-Oxfordian clayrock (France)	6-8 wt.% / 15-18%	700-800 g	4-6 g (11-29% of the total water content)	15 days	Fernández et al. (2009)
	316 Stainless steel (Ø=100 mm)	110 MPa	Quaternary glacial clay-rich till deposits (UK)	15-26%	--	1.6-74 g	0.3 hours-4 days	Hiscock and Najfi (2011)
	Monel-K Ni-alloy (Ø=50 mm, h= 100 mm)	200-500 MPa	Mesozoic shale-rich aquitard sequence (Switz.)	3.8-6 wt.%/ 9-15%	400-500 g	1.4-6.8 g	3-6 days/step	Mazurek et al (2012) Kihō et a. (1999)

Since that time, squeezing has been a mainstay for the collection of pore water. Several groups of Scientifics have developed modifications to the squeezing technique in order to adapt this methodology to specific requirements in their study areas. The designs are usually based on the principles of low- or high-pressure mechanical squeezing (depending on the degree of consolidation of the sediment, i.e., the high or low porosity or high/low water content), followed by filtration. Chronologically, the devices developments can be summarized as follows:

1. At the beginning of the century, the technique was used in agricultural research activities (fertility and salinity) on soil solution chemistry. Morgan (1916) and Burges (1922) summarized the various approaches for obtaining soil solution as drainage waters (lysimetry), soil extracts, artificial roots (suction lysimetry), centrifugation, column displacement, pressure displacement including fluid and hydraulic pressure displacement (soft soils). Manually operated devices (Gola, 1910) and hydraulic presses (Ramann et al., 1916; Lipman, 1918; Burgess, 1922) were used to extract pore fluid from for unconsolidated sediments and soils. Ramann et al., (1916) required 40 kg of very wet soil in eleven to twelve squeezings to obtain 1 liter of pore fluid by using a hydrostatic press at 29.4 MPa. Lipman (1918) used a direct pressure method by using a hydraulic press operated at higher pressures of 294 MPa to extract water from 300-400 g of moist soils of 15-20% moisture. Burgess (1922) applied Lipman's method in soil fertility investigations to obtain the interstitial water composition from sandy-loam soils with moisture contents between 8 and 18%. He obtained around 30-40 mL of water from 400 g of soil, and the analysed calcium and magnesium concentrations did not change with squeezing pressures ranging between 11 and 110 MPa.
2. During the forties, high-pressure linear piston ($L > D$) devices were developed independently in the USSR and in the United States. In the Soviet Union, between the 1930s-1940s, Kryukov and his co-workers were leaders in studying the compaction of Recent sediments and the chemistry of the associated solutions squeezed out. Laboratory compaction and fluid extraction experiments using single-stage, dual-piston or duplex-piston hydraulic squeezers were performed on unconsolidated and consolidated sediments. A practical high load compression stainless steel squeezing device with a self-sealing free gasket was designed by Kriukow (1947) for agronomic and geological purposes, where pore fluids could be easily extracted from both unconsolidated and consolidated sediments. Buneeva et al. (1947) squeezed interstitial fluid from Jurassic claystones containing 9% water by wet weight. From the 1950s onward, Soviet workers used Kriukov-type squeezers to achieve major advances in knowledge of the interstitial chemistry of oceanic sediments (Bruevishc, 1966; Shishkina, 1968). Thick-walled steel squeezers, permitting pressures up to 980 MPa, were used for obtaining fluids from even dense sedimentary rocks. However, the most widely used devices produce pressures from 20 to 69 MPa.
3. During the forties and fifties, mud filter presses, made of stainless steel and using compressed gas or CO_2 to force filtrate through filter paper, were used in the petroleum industry to determine the filtrate loss of drilling fluids, or remove mud filtrates from oil-field drilling muds since their introduction by Richards (1941). Modifications of the filter presses have been used by petroleum engineering for extraction of pore water from drilling muds, materials-processing industry (slurry monitoring) and geotechnology. Analysis of the electrolyte content of clayey muds used in drilling for groundwater, waste disposal, and oil and gas became important in the late 1940s and 1950s when quantitative methods for evaluating geophysical logs in boreholes were developed.
4. In the fifties, triaxial and hydrostatic compaction apparatuses (fluid pressure systems) were used in the petroleum engineering research. Hall (1953) employed hydrostatic pressure cell to study pore-volume changes in sandstone and limestone cores. Fatt (1953) analysed the effect of overburden pressure on permeability. Sholl (1963) used this technique for analyzing the interstitial water chemical composition from coarse-grained sediments. However, until the 70s, high-pressure triaxial cells incorporating the effect of temperature were not developed (Sawabini et al., 1970).
5. In the 1960s, high-pressure dual-piston compaction apparatuses were developed to achieve pressures up to 3500 MPa to analyse solutions from sedimentary rocks (Kryukov, 1961); and in order to study the compressibility of clays (Rieke et al., 1969) and the relationship between pressure and moisture content in clays (Chilingar et al, 1963a,b). The later works were related with the

abnormally high fluid pressures in the less permeable shales in compacted basins, intensely investigated by petroleum geologist and engineers. These equipments utilize the consolidometer principle of two-directional fluid flow while using a dual, linear piston pressure application.

6. Since the late 1950s, the marine sciences during the Deep Sea Drilling Project (1968-1983) have probably led other fields in the sophistication and accuracy with which the best interstitial water measurements have been made in marine sediments by geochemists. In studying the chemistry of interstitial fluids of hydrated clays and “soupy” marine sediments, the problem of extracting such fluids for chemical analysis was solved by various investigators by using a consolidometer. Besides, various inexpensive and portable (to be used in the field and on board ship) filter presses were developed. They were made of stainless steel, plastic or Teflon, some of them thermoregulated, for extracting interstitial water from modern sediments and marine sediments (60-70% water content) at low pressures (2-6.9 MPa). This low pressure squeezer design is based on either a mechanical pressure application: manual turn-screw plunger or screw jack operated by hand (Shepard and Moore, 1955; and Siever, 1962) or a gas pressure system (gas-driven piston) (Gann, 1965; Hartman, 1965; Presley et al., 1967) to achieve the same results.
7. In 1966, Manheim from USGS developed a heavier steel squeezer from the earlier designs of a number of Russian workers, especially Kriukov (1947), to recover interstitial water from more highly indurated oceanic drill-cores (Recent to Palaeocene sediments) during the Deep Sea Drilling Project (Manheim and Sayles, 1974). It was used a standard 10-ton laboratory press (cylinder and ram made by the Carver Co., Summit, N.J.) capable of applying loads up to 150 MPa. The original squeezer used AISI 303 SS cylinder of 28.6 mm inside diameter and 76.2 mm height. The filter unit consists of a stainless steel screen and a perforated steel plate or a sintered disc fitted into a filter holder. Rubber and Teflon disks just below the piston prevent loss of fluid upward when pressure is applied. The water is collected by a syringe, the expulsion of the water being unidirectional. This work confirmed the Soviet experience with similar squeezers that pressure does not appreciably affect the composition of extracted waters when proper precautions are taken into account, i.e., applying safety squeezing pressure limits, below a threshold value determined experimentally for each sediment, in order to avoid squeezing out electrolyte-poor adsorbed water from sediments. Chloride concentration in interstitial waters from typical marine sediments varied less than 1% when extracted by hydraulic squeezer under pressures varying from 3.8 to 80 MPa.
8. From 1980’s generic research programs into the feasibility of underground geological disposal of low, intermediate and high level radioactive wastes in argillaceous formations are being carried out (Savage, 1995). Squeezing technique has been used from 1980-1985 for obtaining pore water from bentonites and consolidated and indurated clayrocks in the context of nuclear waste disposal. High pressure squeezing cells are used to extract fluids from a wide range of clayey materials of low porosity and low moisture content (5-22%) at pressures ranging between 10 MPa and 600 MPa (Table 2). This requires specialist equipment and is not routinely attempted. Most high pressure systems use a hydraulic press and are similar to those designed by Kriukov (1947) and Kriukov and Komarova (1954), and adapted by Manheim (1966).
9. From the ninety’s squeezing technique is also used in multidisciplinary investigations, such as in evaluating the effects of effluent discharges from gold mines on the ecosystem (Mudroch et al., 1994), the release of contaminants from sediment to water or the release of heavy metals in soils affected by pyritic sludges (Alonso et al., 2002), and the study of soils (Table 2) (Shen and Tang, 1992; Di Bonito, 2005; Di Bonito et al., 2008; Böttcher et al., 1997) and aquitards (Hiscock and Najafi, 2011).
10. Krahn and Fredlund (1972) used the squeezing technique at a pressure of 34.5 MPa to obtain osmotic suction measurements on the glacial till and Regina Clay. The osmotic suction of a soil can be indirectly estimated by measuring the electrical conductivity (indicative of total concentration of dissolved salts) of the soil pore water. The measured osmotic suctions were in agreement with the total minus the matric suction measurements. The results also support the validity of the matric and osmotic suctions being components of the total suction.

3. MATERIALS AND METHODS

3.1. Geological Setting

The Opalinus Clay is a relatively stable argillaceous formation of very low permeability, consisting mainly of incompetent, silty and sandy shales, deposited around 180 My (Aalenian). This formation is being analysed in the Mont Terri Rock Laboratory (Figure 2), which is situated in a 3962 m long motorway tunnel in the Jura mountains of north-west Switzerland. Rocks in the Jura mountains are of Triassic to early Cretaceous ages and were deposited mostly in a coastal to shallow marine environment with generally uniform subsidence. They comprise limestones, evaporitic rocks and marls/shales. The Mont Terri Rock Laboratory cuts the Opalinus Clay formation at the south-eastern part of the Mont Terri anticline of the Folded Jura formed during the Late Miocene to Pliocene (10 to 5 My ago). The reconnaissance gallery of the Rock Laboratory intersects a 245 m long section of the Opalinus Clay, which dips from 35° to 55° to the south-east. The main characteristics of Opalinus Clay at Mont Terri can be found in Thury and Bossart (1999) and Bossart and Thury (2008).

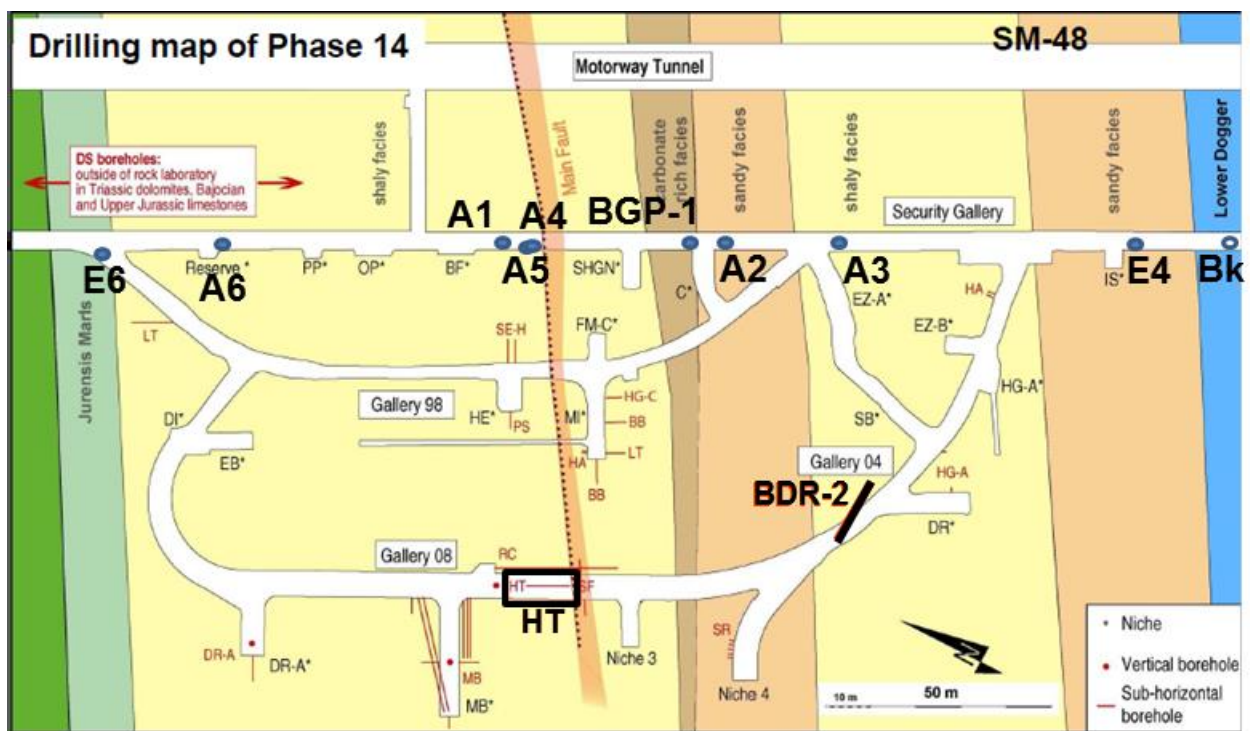


Figure 2. Layout of the Mont Terri Underground Rock Laboratory, showing the sub-divisions of the Opalinus Clay according to lithological facies and the location of the ‘main’ fault, and location of the dedicated boreholes for pore water studies: BWS- A1, A2, A3, A4, A5, A6 (bore water sampling), BHT-1 (Hydrogen Transfer), BDR-2 (Diffusion)

The Opalinus Clay formation can be considered as an overconsolidated shale formation (present overburden 300 m, estimated overburden in the past at least 1000 m). It has an apparent thickness of 160 m (90-m true thickness) and can be divided into five lithostratigraphic subunits, grouped into three main facies: *shaly facies*, *sandy facies* and a thin *carbonate-rich, sandy facies*. These facies can be explained by different sedimentary environments in a shallow coastal basin during the time of deposition. The Opalinus Clay formation is underlain by the Toarcian Jurensis Marl and overlain by the so-called Lower Dogger or Blaukalk (Upper Aalenian/Lower Bajocian).

The Opalinus Clay is characterised by a very low hydraulic conductivity of the rock matrix and tectonic faults (best estimate of $2 \cdot 10^{-13}$ m/s). Advection is thus quite limited and molecular diffusion is the dominant transport process. Of special interest are the concentration profiles of total dissolved solids in the pore water of the Opalinus Clay, with a continuous decrease towards the Lower Dogger formations (from ~ 12 g/L of chloride to ~ 2 g/L of chloride) and a sharp concentration drop in the Upper Liassic formations. The pore water in the Opalinus Clay is a high salinity NaCl water-type. The Br^-/Cl^- and $\text{SO}_4^{2-}/\text{Cl}^-$ ratios are close to the seawater, although these ratios depend on the geographic location of water sampled from the Opalinus Clay formation; i.e., the proximity to the surrounding aquifers (Pearson et al., 2003).

The Opalinus Clay has a complex mineralogy, consisting of variable high contents of sheet silicates, carbonates and quartz. The qualitative mineralogical composition of the Opalinus Clay is similar, particularly in the sandy and shaly facies. The shaly facies contains more clay minerals and less quartz compared to the sandy facies. The carbonate-rich sandy facies contains more calcite and quartz, but less clay minerals. Typical values for the shaly facies are: 66% clay minerals (illite, illite/smectite mixed layers, chlorite and kaolinite), 13% calcite (with also siderite and dolomite/ankerite), 14% quartz, 2% feldspars, 1.1% pyrite, and 0.8% organic carbon. Compared to the shaly facies, the sandy facies contains more quartz (25%) and less clay mineral (50%) (Gaucher *et al.*, 2003).

3.2. Core sample material

Since 1997 seven core samples from boreholes drilled inside the Mont Terri Rock Laboratory has been analysed for characterizing the pore water by the squeezing technique at CIEMAT (Table 3). They belong to boreholes dedicated to water sampling BWS-E6, BWS-A4, BWS-A5, BWS-A6 and BWS-E4 drilled in 1997 and 1998 in the Security Gallery (constructed in 1989). Other cores belong to the boreholes BDR-2 and BHT-1, which are located in the Gallery 98 and the Gallery 08 and drilled in 2005 and 2009, respectively. All the core samples studied correspond to the Shaly Facies, except the cores BWS-E4 and BWS-E6, which belong to the Sandy Facies of the Opalinus Clay and the underlying Jurensis Marl formation, respectively. The location of the boreholes is shown in Figure 2.

It is interesting to note the different techniques used over time for drilling boreholes at Mont Terri trying to avoid disturbances in the composition of the pore water. As example, most of the boreholes focused on geochemistry at Mont Terri were drilled 10-20 m depth by using air as dust evacuation. However, since 2002 the boreholes began to be drilled with N_2 for avoiding possible alterations of the clayrock by oxidation; and since 2009 with Ar gas to prevent modifications of the pore water and rock by oxidation and bacterial disturbances. Thus, the borehole BHT-1 (15 m depth and 76 mm diameter) was drilled inclined upward perpendicular to bedding (dip: $+48^\circ$, azimuth: 140°). The first 9 metres of this borehole were drilled with air as dust evacuation, whereas the last 6 m were drilled with argon gas.

Another difference along the years of investigation was the way of preservation of the drillcore samples for avoiding oxidation and water humidities losses. Instead of using sealed plastic bags, the cores were wrapped in vacuum aluminium coated multilayer polyethylene sheet (190 μm total thickness, water vapour permeability: < 0.04 $\text{g}/\text{m}^2/\text{day}$ at 40°C , 90% R.H.) made of three superimposed layers of polyethylene terephthalate (PET, polyester, 12 μm), aluminium (Al, 12 μm) and polyethylene (LDPE, 165 μm). Nowadays, this technique is combined with stainless steel cells flushed with nitrogen/argon and submitted to partial vacuum, where the wrapped cores are placed inside for long-term storage.

Besides, at the beginning of the Mont Terri Project, the drillcore samples (BWS and BDR) were transported, after borehole survey and core logging for packing, to the workshop located outside the rock laboratory. Then, the cores were wiped to remove any drilling fluid on the surface, placed in aluminium-foil bags flushed with nitrogen gas to displace atmospheric gases and then sealed after applying vacuum. A second layer of aluminium-foil was placed in the same way and finally, the core material was wrapped with durable plastic to ensure full protection of the cores and to avoid moisture losses previous to analyses and squeezing.

Table 3. Characteristics of the core samples from the Opalinus Clay

Core Sample	Facies	Tunnel meter (m)	Borehole drilling date/Length	Specific weight (g/cm ³)	Bulk density _{wet} (g/cm ³)	Dry density (g/cm ³)	Water content _{dry} (%) ⁽³⁾	Water content _{wet} (%)	Physical porosity (%)	Water-loss porosity (%)	Degree of Saturation (%)	Water content at saturation (%)
BWS-E6 m. 3.05-3.40	Jurensis Marl ⁽¹⁾	1022.1 (162.5) ⁽²⁾	Sep. 1998/ 5.15 m	2.697	2.40	2.23	7.8	7.2	17.3	17.4	100	7.8
BWS-A6 m. 4.10-4.30	Shaly facies	1003.5 (150.4)	Sep. 1998/ 20.08 m	2.737	2.46	2.30	7.0	6.5	16.0	16.1	100	6.9
BWS-A4 m. 6.99-9.94	Shaly facies	929.0 (113.2)	Sep. 1997/ 10.34 m	2.748	2.45	2.28	7.5	7.0	17.0	17.1	100	7.5
BWS-A5 m. 7.40-7.79	Shaly facies	930.0 (107.1)	Sep. 1997/ 10.10 m	2.743	2.46	2.30	7.0	6.5	16.2	16.1	100	7.0
BHT-1 m. 12.4-12.9	Shaly facies	(109.7)	April 2009/ 15 m	2.720	2.43	2.26	7.5	7.0	16.9	17.0	100	7.5
BDR-2 m. 5.93-6.36	Shaly facies	(59.1)	May 2005/ 12.3 m	2.713	2.45	2.29	6.8	6.4	15.6	15.6	100	6.8
BWS-E4 m. 4.28-4.65	Sandy facies	794.2 (12.8)	Sep. 1998/ 5.10 m	2.698	2.45	2.31	6.2	5.8	14.4	14.3	100	6.2

⁽¹⁾ Liassic limestone formation which underlay the Opalinus Clay

⁽²⁾ In parenthesis: Distance from the boreholes to Dogger formation

⁽³⁾ Dry conditions: oven-heating at 110°C

However, this practice was changed since 2006. Thus, in the case of the drillcores from boreholes BDR-2 and BHT-1 (Table 4), the rock samples were packed inside the Mont Terri rock laboratory immediately after their recovering by placing them in aluminium-foil bags (Figure 3), which were flushed with argon gas to displace atmospheric gases and sealed after applying vacuum. A second layer of aluminium-foil was placed in the same way. Finally, the core material was put inside PVC tubes, which were flushed with argon and sealed, to ensure full protection of the rock material. At CIEMAT laboratories, the PVC tubes with the rock samples were vacuum packed in Al-coated polyethylene sheets, and stored in a refrigerator at 4°C to avoid micro-organisms growth.

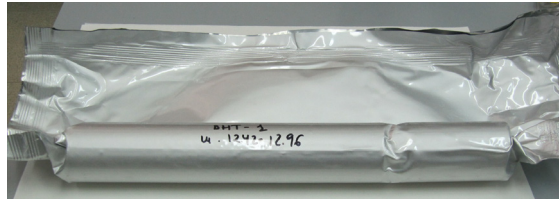


Figure 3. Preservation of the core sample BHT-1/27 from the borehole BHT-1

Table 4. Characteristics of the collection and preservation of core samples and squeezed waters

Core Sample	Borehole drilling	Drillcore preservation	Water collection
BWS-E6			
BWS-A6		Two Al coated	
BWS-A4	Drilling using air as dust evacuation	multilayer polyethylene PE sheets at vacuum put outside the tunnel	Ambient conditions Inside a Syringe
BWS-A5			
BWS-E4			
BDR-2	Air Drilling	Two Al coated multilayer polyethylene PE sheets at vacuum put close to the borehole inside the tunnel	Ambient conditions Inside Sealed vacuum vials flushed with Ar
BHT-1	0-9 m: air drilling 9-15 m: Argon drilling		

3.3. Physical properties

The gravimetric water content, *w.c.*, is defined as the ratio between the weight of water and the weight of dry solid expressed as a percentage. The weight of water was determined as the difference between the weight of the sample and its weight after oven drying at 110°C for 24 hours (weight of solid), and the following relationships were used:

$$WC_{wet} = \frac{WC_{dry}}{(1 + WC_{dry})} \quad \text{Eq. 2}, \quad WC_{dry}(\%) = \frac{M_w}{M_{dry}} \times 100 \quad \text{Eq. 3}$$

where, WC_{dry} is the gravimetric water content on a dry mass basis of the rock; M_w is the mass of water in the rock, and M_{dry} is the mass of rock dried at 110°C for 24 hours.

The water content at saturation was obtained according to:

$$wc_{sat}(\%) = \frac{\rho_w}{\rho_d} - \frac{\rho_w}{\gamma_s} \quad \text{Eq. 4}$$

where, ρ_w is the density of the pore water (assumed to be 1.0 g/cm³), γ_s is the specific gravity of the solid sample, and ρ_d is the bulk dry density.

Dry density, ρ_d (g/cm^3) is defined as the ratio between the weight of the dry sample and its volume prior to drying. The volume of the specimens was determined by immersing them in a recipient containing mercury and by weighing the mercury displaced, as established in UNE Standard 7045 “Determination of soil porosity”.

The specific gravity of the solid particles, γ_s , commonly referred as grain density (g/cm^3), is defined as the relation between the weight of the solid and its volume occupied. Specific gravity (addimensional) was determined by pycnometry using water, according to the UNE Standard 103-302: “Determination of the relative density of soil particles”. In this method, the weight of the water displaced by a known mass of oven-dried and degassed soil is determined.

The physical porosity or total porosity was calculated by means of the relationship:

$$n = 1 - \frac{\rho_{\text{bulk,dry}}}{\gamma_s} \quad \text{Eq. 5}$$

where, $\rho_{\text{bulk,dry}}$ is the bulk dry density, and γ_s is the grain density or specific gravity.

The volumetric moisture content or water-loss porosity, θ , which is the ratio of water-filled pore space to total volume ($V_{\text{wat}}/V_{\text{tot}}$); and the saturation degree, S , which is the ratio of water-filled to total volume ($V_{\text{wat}}/V_{\text{pores}}$), were calculated from the equations:

$$\theta = \frac{WC_{\text{wet}} \cdot \gamma_s}{WC_{\text{wet}} \cdot \gamma_s + (1 - WC_{\text{wet}}) \cdot \rho_w} \quad \text{Eq. 6} \quad \text{or} \quad \theta = WC_{\text{dry}} \times \rho_{\text{bulk,dry}} \quad \text{Eq. 7}$$

$$S = \frac{\theta}{n} \quad \text{Eq. 8}$$

where, n is the total or physical porosity, which is the ratio of the pore volume to the total volume ($V_{\text{pores}}/V_{\text{tot}}$); and ρ_w is the density of the pore water.

3.4. Soluble salts by aqueous leaching

The soluble salts were analysed in aqueous extract solutions. Prior to the test, the subsamples were crushed without previous drying at ambient conditions with minimal atmospheric contact, except the core sample BHT-1 which was crushed inside an anoxic glove box under anoxic conditions.

The powdered rock samples were placed in contact with deionised and degassed water at different solid to liquid ratios (1:1, 1:2, 1:4, 1:8 and 1:16), shaken end-over-end and allowed to react for two days under anoxic conditions inside an anoxic glove box with atmosphere oxygen content below 1 ppm. After phase separation by centrifugation (30 minutes at 12500 rpm), the supernatant solutions were filtered by a 0.45 μm pore-size syringe filter (inside the anoxic glove box) and analysed.

3.5. Total Cation Exchange and Cation Exchange Population

Two methods were used to determine the total cation exchange capacity (CEC): a) sodium acetate at pH=8.2 method, and b) Copper triethylenetetramine method (Ammann et al., 2005). In the first one, the exchange sites of 2.5 g of rock sample were saturated with sodium by means of three successive washing with 1 M sodium acetate at pH=8.2 (33 mL each time). The adsorbed sodium was then displaced by successive extractions with NH_4NO_3 or NH_4AcO 1 M at pH 7.0. The analytical error for this determination is around $\pm 5\%$. In the second method, 200 mg of clayey sample were mixed with 25 mL of deionized water and the suspension was dispersed by ultrasonic treatment for 5 min. Then, 10 mL of 0.01 M $[\text{Cu}(\text{trien})]^{2+}$ were added and allowed to react by end-over-end shaking for 1 hour. Afterwards, the suspensions were centrifuged at a constant rotation speed of 15500 rpm for 20 min. The supernatant solution was filtered through a 0.45 μm syringe-filter. 3 mL of the clear blue solution were filled into 1 cm optical glass cuvettes and the adsorption of the solution was measured

spectrophotometrically at a wavelength of 578 nm by using a Spectroquant UV-Vis spectrophotometer from Merck and deionized water as a blank solution. Prior to the tests, a calibration curve to calculate the Cu-Trien concentration was determined from a series of dilute Cu(II)-triethylenetetramine solutions (0.003 M; 0.002 M; 0.001 M; 0.0003 M; 0.0001 M).

The determination of the cation Exchange population was performed by using Cs as index cation (Sawhney, 1970). Solid samples were equilibrated at 1:4 solid to liquid ratio (0.25 kg/L) with 0.5 M CsNO₃ at pH 8.2. After phase separation by centrifugation at 15500 rpm for 20 min, the supernatant solutions were filtered through 0.45 µm and the concentrations of the major cations were analysed.

3.6. Pore water obtained by squeezing

The pore water of the clayey rock samples was obtained by the squeezing technique at high pressures. At CIEMAT the squeezing ring (Fernández et al., 2001; Fernández et al., 2003; Fernández, 2004) is similar to that developed by Peters et al. (1992) and Entwisle and Reeder (1993). The squeezer has been designed to allow a one-dimensional compression of the sample. An automatically controlled hydraulic ram squeezes the content of the cell vertically upwards and the expelled pore water crosses through a stainless steel filter/support at both ends of the cell (Figure 4). Expelled water was collected inside a polypropylene syringes (in the case of BWS cores) or sealed vials (for BDR-2 and BHT-1 cores) after passing through a sintered micro-filter located inside the squeezer device (Table 4). The compaction chamber is made of type AISI 329 stainless steel (selected due to its high tensile strength and resistance to corrosion) with an internal diameter of 70 mm. The compaction chamber is 500 mm high with 45 mm wall thickness, allowing pressures up to 200 MPa. The hydraulic ram was operated to exert a maximum stress up to obtain some mL of water sample for chemical analysis, which depended on the characteristics of each core sample analysed.

The filtration system allows the extraction of interstitial water by drainage at the top and at the bottom of the sample. This system comprises a 0.5 µm stainless steel AISI 316L sintered porous disk (Cr 17.36%, Ni 11.4%, Mo 2.15%, Si 0.94%, Mn 0.17%, C 0.027%, S 0.011%, P 0.022%, Fe 66.92%) in contact with the sample. The liquid is collected through stainless steel tubes (¹/₁₆ inch) in a syringe or a vacuum vial sealed by a septum. The whole system remains under ambient conditions (room temperature of about 20-22°C) and not under anoxic atmosphere. However, in the case of cores from boreholes BDR-2 and BHT-1 (Table 4), before starting the test the squeezing cell with the core sample inside was flushed with Ar (or N₂) prior to the loading of the sample to remove all the air and avoid any possible oxidation of the sample during the test. Besides, the sealed vials for water collection were also flushed with Ar (see Figure 4b) prior to start the squeezing test to prevent the oxidation of the water sample.

The core samples for squeezing were prepared using a knife to scrape the outer annulus of the core in order to discard possible material contaminated by the drilling fluid. Each sample was trimmed in separate pieces, fragmented ideally to lumps fitted to the squeezing cell or small pieces of about 25-200 grams. The total sample was weighed and placed into the body of the cell. A small stress of 1 to 10 MPa was initially applied to remove most of the atmospheric gas from the cell and allow the sample to bed in. The applied stress progressively increased up to the selected pressure, rather than in a single step. This avoids overconsolidation or collapse of the clay-pore system. Then, a syringe was assembled to collect the squeezed water, except in the case of the BDR-2 and BHT-1 squeezing tests, for which a vacuum septum vial was used. When the maximum of squeezed water was obtained, the syringe or vial was removed from the device, keeping the sample away from any contact with the atmosphere by wrapping the syringe or the septum vial with Parafilm®. The sample collected was weighed and stored in a refrigerator at 4°C before chemical analyses, in order to prevent unwanted bacterial activity. In all experiments, the final mass, water content and dry density of the squeezed cores were determined at the end of the tests.



Figure 4. a) Squeezed water extraction apparatus used at CIEMAT; b) Flushing of the squeezing cell and the sampling vial with argon gas prior to the squeezing test; c) pieces of the squeezer

3.7. Water chemical analyses

The water samples were filtered through 0.45 μm syringe filters inside an anoxic glove box, except those for pH and E.C measurements. The pH was measured by means of an ORION 720A pH-meter equipped with a Metrohm 6.0234.100 pH combination electrode. Merck pH buffer solutions of pH 4.00 and 7.00 were used for pH-meter calibration. Electrical Conductivity measurements (EC) were performed by means of an ORION 115 conductimeter. The conductivity cell was checked/calibrated with a standard solution of 12.6 mS/cm (NaCl). The measurements were automatically adjusted to a temperature of 25 $^{\circ}\text{C}$.

The total *alkalinity* of the water samples (expressed as mg/L of HCO_3^-) was determined with a specific Dynamic Equivalence point Titration (DET) method for analysing samples of 1-2 mL. The instrumentation consists on a Metrohm 785 Titroprocessor equipped with a 5 mL burette 685 Dosimat and a 6.0224.100. Metrohm combined pH micro-electrode.

The *major and trace cations* were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) in a Jobin Yvon JY48+JY38 spectrometer. Sodium and potassium were determined by flame atomic emission spectrometry, FAES, in a Perkin Elmer 2280 spectrometer, and *ultratrace elements* were determined by ICP-MS (Finningan Mat SOLA).

Anions were analyzed by ion chromatography (Dionex DX-4500i). Soluble *silica* was determined using a UV-VIS spectrophotometer by means of the reduced molybdosilicic acid (EPA 370.1 Method) if an aliquot higher than 5 mL was obtained. Otherwise, the ICP-AES technique was used. An ORION 901 microprocessor ion-analyzer, equipped with ion selective electrodes, has been employed for F⁻ and I⁻ determination. Fe(II)/Fe(III) ratio was determined by UV-Vis spectrophotometry with the ferrozine method after acidification of the samples to pH<1 with HCl. It was estimated that the analytical error for major ions was ±5% (including necessary dilution steps), except for K, Fe and alkalinity whose analytical error was ±10-20%.

4. RESULTS

4.1. Physical properties

The Opalinus Clay is an indurated cryptocrystalline mudrock of fine-grained nature and with a complex mineralogy. The cores are dark-gray colour clay, with a quite homogeneous texture, and presented some carbonate lens. The main core physical characteristics of the core sample analysed are shown in Table 3, which are in agreement with those of reference Opalinus Clay samples described in Pearson et al. (2003) and Bossart and Thury (2008). In Opalinus Clay rock samples the gravimetric water content ranged between 6.2 and 7.5% (calculated by drying the sample at 110°C). The grain density ranged from 2.698 to 2.748 g/cm³, and the dry density between 2.26 and 2.31 g/cm³; being the average values for grain density and dry density of 2.727 and 2.29 g/cm³, respectively. According to these data, the physical porosity in Opalinus Clay is between 14.4 and 17.0 vol.%, and is equal to water-loss porosity. Therefore, the degree of saturation of the core samples is 100%, i.e., the drillcore samples are fully saturated, equal to the rock conditions in the whole formation. This indicates a very good conservation of the core material during their transport from Mont Terri to the laboratory and until the analyses.

4.2. Soluble salts by aqueous leaching

Aqueous leaching experiments were performed with the purpose of determining the inventories per mass of rock for conservative or free anions such as chloride and bromide. For BWS-xx core samples (xx being the number of the borehole) drilled during 1998 and 1999, aqueous extractions were carried out on a series of rock samples at different solid to liquid (S:L) ratios under ambient conditions. However, in BDR-2 and BHT core samples aqueous leaching was performed under controlled N₂ atmosphere inside an anoxic glove box (<1 ppm atmospheric O₂) in order to minimize oxidation of pyrites (1 to 3 wt.% in the whole rock). The concentration of soluble ions was measured by mixing powdered rock material and deionised, free-air water as a function of the S:L ratio (1:1, 1:2, 1:4, 1:8 and 1:16). The results obtained are shown in Table B. 1 and Table B. 2 from the Electronic Appendix. As it would be discussed later, the composition of an aqueous extract solution is not representative of the pore water due to the dilution and dissolution processes, the variation of cations and some anions being non-linear as a function of the solid to liquid ratio (or with the inverse of the water content). Leaching results will be only used in this work for obtaining the chloride and bromide inventories of the rock and analysing possible water-rock interaction processes.

4.3. Cation Exchange Capacity (CEC) and Cation Exchange Population

The CEC and cation exchange population determined in the different core samples are shown in Table 5. CEC ranges from 10 to 14 meq/100g, the lowest value being found in the BWS-E4 sample belonging to the Sandy facies of the Opalinus Clay. No significant differences in values were found with the two methods used for CEC determination: the NaOAc/NH₄OAc and Cu-trien methods. Regarding cation exchange population, the main exchangeable cation is sodium, followed by calcium/magnesium and potassium. Strontium and barium are also present at much lower contents.

Table 5. Total exchange capacity and cation exchange occupancies, in meq/100g

Core Sample	Na	K	Mg	Ca	Sr	Ba	Σ cations	Total CEC ⁽³⁾
BWS-E6⁽¹⁾ m. 3.05-3.40	6.42 ±0.15	0.93 ±0.05	3.29 ±0.29	7.61 ±0.53	0.13 ±0.01	0.003 ±0.001	18.38 ±1.03	11.7 ± 0.3
BWS-A6⁽¹⁾ m. 4.10-4.30	6.52 ±0.01	0.90 ±0.01	3.19 ±0.15	7.24 ±0.35	0.11 ±0.01	0.002 ±0.001	17.95 ±0.50	12.6 ± 0.1
BWS-A4⁽¹⁾ m. 6.99-9.94	3.85 ±0.87	0.91 ±0.13	2.76 ±0.33	5.40 ±0.50	0.08 ±0.01	0.002 ±0.001	13.0 ±1.0	12.9 ± 2.3
BWS-A5⁽¹⁾ m. 7.40-7.79	3.02 ±0.08	0.76 ±0.01	2.17 ±0.07	4.75 ±0.09	0.07 ±0.01	0.001 ±0.001	10.8 ±1.0	11.6 ± 1.1
BHT-1⁽²⁾ m. 12.4-12.9	5.49 ±0.01	3.07 ±0.01	2.79 ±0.46	2.85 ±1.12	0.95 ±0.03	0.025 ±0.001	14.3 ± 1.6	13.2 ± 1.0
BDR-2⁽²⁾ m. 5.93-6.36	4.68 ±0.22	2.43 ±0.03	2.63 ±0.09	2.95 ±0.37	0.18 ±0.01	0.001 ±0.001	12.9 ± 0.1	14.4 ± 0.7
BWS-E4⁽¹⁾ m. 4.28-4.65	3.15 ±0.01	0.93 ±0.05	2.88 ±0.01	5.93 ±0.09	0.25 ±0.01	--	13.13 ±0.14	9.0 ± 1.1

⁽¹⁾ Cation exchange occupancies determined with the NH₄OAc method at pH=8.0 after leaching the soluble salts. Therefore, calcium concentration is overestimated and Na underestimated.

⁽²⁾ Cation exchange occupancies determined with the CsNO₃ method at pH 8.2. Potassium may be overestimated due to the high affinity of Cs for illite that would displace more K than expected.

⁽³⁾ CEC determined with the NaOAc/NH₄OAc method.

4.4. Pore water chemistry extracted by squeezing

Two types of squeezing tests were performed with Opalinus Clay core samples: one of them was aimed for obtaining water for analysing the chemical composition of the pore water. To this type of tests belong the core samples from boreholes BWS-E4, BWS-A6, BDR-2 and BWS-E6. The squeezing tests on the core samples BWS-E4, BWS-A6, and BWS-E6 were performed in 1999, and on the BDR-2 rock sample in 2009. The other type of tests was aimed for studying the influence of the squeezing pressure in the chemistry of major ions and possible filtration. For this purpose, three squeezing tests were performed: two of them in 1998 (BWS-A4 and BWS-A5 core samples) and another one (BHT-1 core sample) in 2009 (Table 6).

Squeezing tests were carried out from core samples stored after borehole drilling within periods ranging from one month to nine months, except the sample BDR-2 stored during 47 months, which allowed to evaluate the preservation of the core during a long-term storage.

4.4.1. Minimum squeezing pressure for Opalinus Clay core samples

At the beginning of the experiment, the hydraulic ram was operated to exert a maximum stress up to obtain some millilitres of water for chemical analysis, which depended on the characteristics of core sample analysed. In the case of the core sample from the borehole BWS-E6 and BHT-1, the squeezing pressure applied to obtain a first aliquot of pore water was of 70-75 MPa. In the case of the other samples the minimum squeezing pressure ranged between 89 and 150 MPa, being the highest pressure used in the core sample containing a higher amount of carbonates and quartz, as well as a higher dry density and the lowest water content (BWS-E4). In the case of analysing the change in composition with pressure, after the initial pressure value, the squeezing pressure was increased in several steps up to 200 MPa (Table 7).

Pore water extraction by squeezing was successful in samples with water contents ranging between 6.2% and 7.8 %, being 1-2 mL the minimum amount of water required for a complete chemical analysis for major ions. The mass used to carry out the test ranged between 675 and 1600 g, and the total volume of water extracted was between 2 and 12 mL, depending on the final pressure. The total amount of water collected at 75 MPa for Opalinus Clay ranged between 2 and 5 mL. The tests had a total duration between 8 and 32 days for performing a single chemical analysis or up to around 179 days if the pressure was increased in steps up to 200 MPa (Table 6). The time of each test depended on the initial water content of the core sample. For example, for the core BWS-E6 with a water content of 7.8%, only eight days were needed for obtaining 5.5 mL of water. However, about 15 days were usually necessary for obtaining 2-5 mL of water in a squeezing test with this type of clayey material. It must be taken into account that the water flows through the material as a function of the very low permeability of the material. Opalinus Clay core samples are stiffer materials of low permeability and require long periods of squeezing and high squeezing pressures.

The theoretical amount of water that is possible to extract from the core samples has been compared with the extracted water in the way of efficiency (Table 6). In order to evaluate the efficiency in the methodology for pore water extraction two types of criteria have been adopted (Entwisle and Reeder, 1993). One of them allows to evaluate the amount of water for chemical analysis, and control the water losses by the tubes and filters, and can be calculated according to the equation:

$$\text{Efficiency (\%)} = 100 \times \left(\frac{\text{collected water}}{\text{extracted water}} \right) = 100 \times \frac{\text{collected water}}{(\text{initial weight} - \text{final weight})} \quad \text{Eq. 9}$$

The other one evaluates the water volume extracted in relation to the total volume of water available in the core sample, and it is calculated with the following relationship:

$$\text{Total Efficiency (\%)} = \frac{100 \times \text{collected water}}{\text{initial weight} - \text{final weight}} \quad \text{Eq. 10}$$

Total efficiency depends on the maximum load applied. It is interesting to note that only between the 11% and 37% of the total water in the rock was extracted at the end of a squeezing test, even at 200 MPa, i.e., between 60% and 90% of the initial water in the sample (calculated by the weight of oven-dried sample at 110°C) remains in the sample after squeezing.

Table 6. Characteristics of the squeezing tests performed with core samples from the Opalinus Clay

Core Sample	Initial Date	Time lasted between drilling and squeezing (days)	Initial mass (g)	Initial w.c (%)	Final ⁽¹⁾ w.c (%)	Final dry density (g/cm ³)	Squeezing Pressure (MPa)	Time elapsed (days)	Porewater extracted (g) ⁽²⁾	Water collected (g) ⁽³⁾	Final mass (g)	Efficiency (%) ⁽⁴⁾	Total Efficiency (%) ⁽⁵⁾
BWS-E6 m. 3.05-3.40	26/04/1999	210	1500.0	7.8	7.1	2.22	75	8	13.0	5.5	1487.0	42.3	12.0
BWS-A6 m. 4.10-4.30	08/04/1999	197	1486.6	7.0	6.3	2.26	100	15	11.3	2.9	1475.3	25.7	11.6
BWS-A4 m. 6.99-9.94	29/12/1997	96	1055.2	7.5	5.6	2.31	89 to 150	78	8.1	4.0	1047.1	50.0	11.0
BWS-A5 m. 7.40-7.79	07/07/1998	286	1500.0	7.0	5.1	2.34	89 to 200	149	32.4	12	1467.6	37.0	33.0
BHT-1 m. 12.42-12.96	05/06/2009	45	718.4	7.7	4.8	2.34	75 to 200	179	19.0	9.9	699.4	52.2	37.1
BDR-2 m. 5.93-6.36	04/06/2009	1465	675.6	6.8	5.6	2.27	125	13	8.1	3.0	667.5	37.0	19.0
BWS-E4 m. 4.28-4.65	05/03/1999	158	1600.0	6.2	5.2	2.31	150	32	16.0	2.0	1584.0	12.5	17.1

⁽¹⁾ After squeezing (at equilibrium with the final squeezing pressure);

⁽²⁾ Weight loss after squeezing;

⁽³⁾ Water losses are expected due to retained water inside filters and tubings;

⁽⁴⁾ Efficiency (%) = (Collected water x 100)/Extracted water;

⁽⁵⁾ Total Efficiency (%) = (100 x extracted water)/(Initial mass – Dry mass)

Table 7. Summary of the applied pressure, time and extracted water in the squeezing tests with the BWS-A4, BWS-A5 and BHT-1 core samples

BWS-A4 m. 6.99-9.94			BWS-A5 m. 7.40-7.79			BHT-1 m. 12.42-12.46		
Pressure (MPa)	Time (days)	Volume (g)	Pressure (MPa)	Time (days)	Volume (g)	Pressure (MPa)	Time (days)	Volume (g)
25	15	--	37.5	20	--	25	--	--
37.5	8	--	50	7	--	70	5	0.5
50	7	--	62.5	10	--	75	19	2.5
62.5	5	--	70	17	--	100	14	1.8
70	7	--	75	7	--	125	18	1.8
75	8	--	87.5	8	0.1	150	62	1.0
87.5	15	2.0	100	9	0.3	175	21	1.8
100	13	2.0	125	12	3.0	200	40	1.0
			150	13	3.0			
			175	18	3.0			
			200	28	3.0			
Total	78 days	4 g	Total	149 days	12 g	Total	179 days	10 g

4.4.2. Pore water composition as a function of the squeezing pressure: optimal pressure range for determination of Chloride concentration

Three tests were performed on samples BWS-A4, BWS-A5 and BHT-1 in order to evaluate the possible changes in pore water chemistry as a function of the applied pressure; i.e, to analyse possible ionic ultrafiltration or anion exclusion processes when the pore size of the clay material decreases due to high pressures. The increments of applied pressure ranged from 25 to 200 MPa. The pressure steps, time and volume of pore water extracted in each pressure step are shown in Table 7. The water collected at each pressure corresponds to steady state conditions for each applied pressure, i.e. the pressure only is increased when there were no changes in the volume of the sample and the maximum amount of water was obtained at that pressure step.

The chemical composition of the pore waters obtained in all the squeezing tests is shown in Table 8 Table 9 and Figure 5 for BHT-1 core sample. In the squeezed waters from all core samples no significant variations in chloride concentration was observed within the investigated range of pressures (75-200 MPa). Slight variations in the bromide concentration are related to the analytical error of the technique used (IC). Because of the high salinity of these pore water samples (~ 0.35 M), the water aliquot must to be diluted for ion chromatography analysis. Regarding sulfate, the concentration increased with pressure. However, this is related to an oxidation process of pyrite in the cores with time because of the long-time taken for the squeezing study as a function of pressure.

Table 8. Variation of the chemical composition of the pore water with the squeezing pressure in the core samples BHT-1 m. 12.42-12.96 and BDR-2 m. 5.93-6.36

Core sample	BHT-1 m. 12.42-12.96						BDR-2 m. 5.93-6.36
	75	100	125	150	175	200	125
Sq. Pressure (MPa)	75	100	125	150	175	200	125
Vol. Extracted (mL)	2.5	1.8	1.8	1.0	1.8	1.0	3.0
pH	7.7	7.3	7.04	6.0	6.3	6.0	7.3
Cl (mg/L)	9800	10000	9800	9900	9900	10000	6100
SO ₄ ²⁻ (mg/L)	1700	1800	1900	2100	2100	2200	1300
Br ⁻ (mg/L)	30	30.5	30	30	29	29	19.5
NO ₃ ⁻ (mg/L)	< 5	10.8	< 5	< 2	5.0	39	3.4
Alkalinity (meq/L)	1.82	2.20	4.54	n.d.	2.10	n.d.	1.50
SiO ₂ (mg/L)	6.85	6.42	5.13		9.84	9.20	4.06
Na (mg/L)	5400	5500	5400	5500	5500	5400	3300
K (mg/L)	55	51	36	31	70	17	20
Ca (mg/L)	673	610	631	650	630	690	465
Mg (mg/L)	540	490	522	560	540	550	247
Sr (mg/L)	45	40	43	45	45	46	50
Fe (mg/L)	< 0.3	≤ 0.3	0.56	< 0.70	< 0.38	2.5	≤ 0.3
Al (mg/L)	< 0.3	< 0.3	< 0.3	< 0.70	< 0.70	≤ 0.80	< 0.3
B (mg/L)	3.8	3.9	10	5.1	6.8	7.0	3.3
Cu (mg/L)	0.80	< 0.3	0.42	< 0.70	< 0.38	< 0.80	< 0.3
Mn (mg/L)	3.2	1.1	1.0	1.4	1.5	1.2	0.64
Mo (mg/L)	0.78	0.95	0.72	0.76	0.93	1.0	0.55
Ni (mg/L)	0.72	< 0.3	0.31	< 0.70	0.52	< 0.80	≤ 0.3
Ba (mg/L)	< 0.3	< 0.3	0.30	< 0.70	< 0.38	< 0.80	< 0.3
Cd (mg/L)	< 0.3	< 0.3	< 0.3	< 0.70	< 0.38	1.3	< 0.3
Zn (mg/L)	< 0.3	< 0.3	1.1	1.2	0.75	< 0.80	26
E.N. (%)	0.42	-1.46	-0.02	-0.40	-1.08	-2.20	-2.91
E. C. (μS/cm)	31544	31226	31132	31965	31774	31623	18955
E. C. (μS/cm) pH _{free}	28160	28514	28634	28554	28618	28714	17893
Ionic Strength	0.34	0.35	0.35	0.35	0.35	0.35	0.21

Table 9. Variation of the chemical composition of the pore water in the core samples from the boreholes BWS-E6, BWS-A6, BWS-A4, BWS-A5 and BWS-E4

Core sample	BWS-E6 m. 3.05-3.40	BWS-A6 m. 4.1-4.3	BWS-A4 m. 6.99-9.94		BWS-A5 m. 7.40-7.79				BWS-E4 m. 4.28-4.65
Sq. pressure (MPa)	75	100	87.5	100	125	150	175	200	150
Water extracted (mL)	5.5	2.9	2	2	3.4	3	3	3	2
pH	6.8	6.9	7.2	7.3	7.6	7.8	7.8	7.2	8.1
Cl (mg/L)	11000	12000	9500	9500	10000	10000	10000	11000	2500
SO ₄ ²⁻ (mg/L)	1500	1700	4300	4000	4600	4000	4200	3800	2500
Br ⁻ (mg/L)	34.0	35	33	36	34	31	32	36	7.0
NO ₃ ⁻ (mg/L)	1.6	4	3	< 3.0	--	4.1	4.6	4.2	11.0
Alkalinity (meq/L)	0.66	1.61	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.94
Na (mg/L)	6450	6200	6000	5900	6350	6000	6200	6550	2100
K (mg/L)	60	69	92	85.9	78	65	51	70	48
Ca (mg/L)	665	925	1200	1025	710	720	695	790	235
Mg (mg/L)	595	950	750	710	515	480	490	620	255
Sr (mg/L)	45	46	51	57	39	38	38	56	45
Ba (mg/L)	0.2	0.44	< 1.0	< 1.0	< 0.4	< 0.4	< 0.4	< 0.3	< 0.3
Charge Balance (%)	3.49	2.99	4.54	3.09	-2.87	-3.89	-3.25	-1.38	-0.84
E.C. (µS/cm)	31471	33304	30066	29645	30766	30042	30369	32394	10651
Ionic Strength	0.39	0.43	0.41	0.39	0.39	0.38	0.38	0.41	0.14

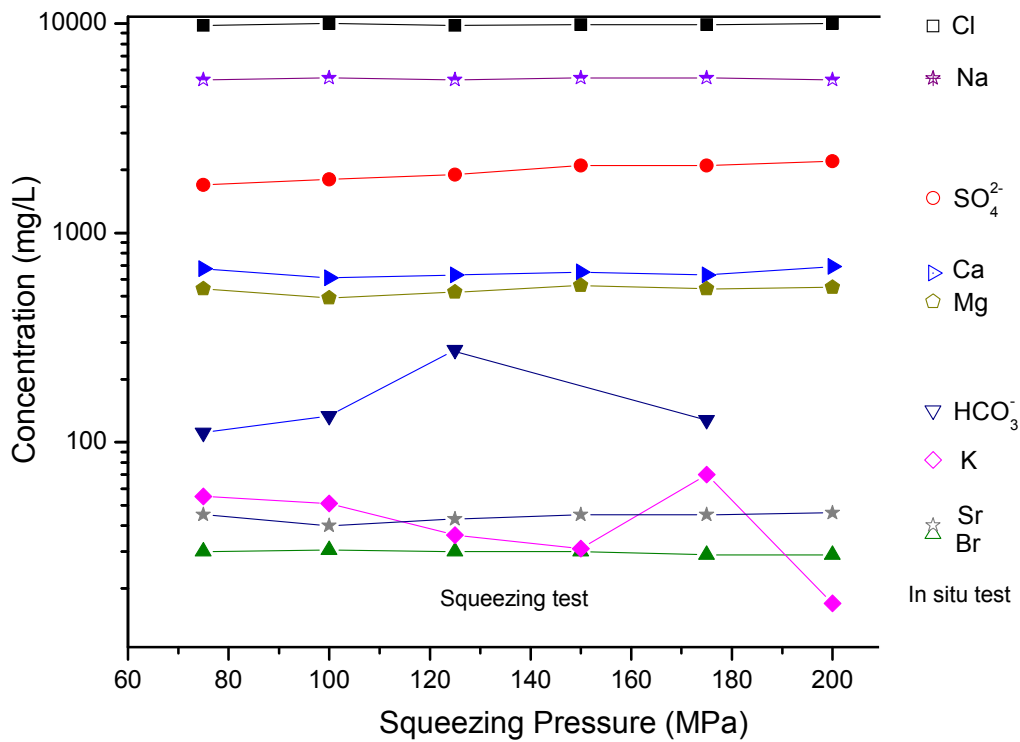


Figure 5 Variation of the chemical composition of the pore water as a function of applied pressure in the core sample BHT-1

5. DISCUSSION

The squeezing studies of the Opalinus Clay core samples performed in the context of the “Geochemical Modelling Task” from the Mont Terri Project for over more than 15 years have allowed to validate and to check the representativeness and the reproducibility of the squeezing technique for the analysis of the ion and isotope data in the pore waters.

The ideal way to validate and demonstrating the veracity of a technique for obtaining the reliable pore water is to perform a comparative study with a direct measurement of a natural pore water from that clayey sediment/rock. However, to separate the natural pore water solution from its harboring solid phase is difficult and sometimes impossible. Other methods would be: a) to check the good reproducibility of the method, and b) to analyse the factors and possible artefacts which could influence on the reliability of the pore water chemical composition extracted by squeezing, such as: 1) rock sampling: decompressional effect, water loss and oxidation, 2) handling, preservation, storage period and conditions prior to extraction of interstitial waters, 3) temperature elevation during core extraction (drilling) and interstitial waters extraction through squeezing, 4) pressure exerted during squeezing, 5) degassing, and 6) oxygen contamination during extraction of pore waters. All these approaches are discussed in this section.

5.1. Squeezed pore waters versus True pore solution: the good, the bad and the ugly

Pore water extraction from clay sediments, clayrocks and soils dates back more than 115 years, and although *in situ* measurements have shown a real development in the past 10 years, the pore water sampling and analysis from core samples remains essential in understanding the clay-rock and water-clay-mineral surface interactions.

Although different studies have shown that, so long as core sample collection, handling and preservation methods are satisfactory, pore waters obtained by squeezing tend to be representative of *in situ* conditions when compared to chemical composition of pore waters obtained by other methods (e.g., packered-borehole waters at *in situ* test); this technique is severely and somewhat caustically criticized and usually is thought that the solution obtained under great pressures would be of doubtful value. However, comparative studies indicate the opposite. Indeed, Manhein in 1974 claims that “existing experience with pressure squeezers or other comparative extraction studies is dealt with in a grossly inadequate way”. For example, Northrup’s paper (1918) is cited in the context that obtaining the true soil solution with squeezing is not a representative method. However, Northrup only suggest that: 1) many bacteria are destroyed by high pressures (172-690 MPa), 2) enormous pressures influence solubilities and the whole physico-chemical equilibrium of the real solution, and 3) the method should be compared with other methods. Besides, Burgess (1921), answering to Northrup’s suggestions substantiated by fact that in sandy loam soils pressures between 11 to 110 MPa had no measurable effect on soil solubility.

Apart from problems which are common in other extraction methods, even in *in situ* tests (oxidation, degassing, changes in temperature, etc.); squeezing technique could add intrinsic problems for what it has been criticized (Von Engelhardt and Gaida, 1963; Siever et al., 1965): a) squeezing pore waters would be diluted due to come out the of double-layer water, b) possible existence of membrane or filtering effect through charge-net clay membranes in highly consolidated sediments, and c) exclusion of dissolved substances in the structure of water in the boundary layer.

Extensive studies of squeezing as a pressure filtration system have been performed over time. Soviet authors (Kryukov and Zhuchkova, 1963; Shishkina, 1972; Manheim, 1966; and Sayles, 1970, 1979) demonstrated that pressure does not appreciably affect the composition of extracted waters when proper precautions are taken into account, such as applying safety squeezing pressure limits, below a threshold value determined experimentally for each sediment, in order to avoid squeezing out electrolyte-poor adsorbed water from sediments (double-layer adsorbed water retained by Donnan forces), extracted pore water being a mixture of the true pore water and the outer layers of the double-layer water. Above those pressures, adsorbed water having lower (not higher) electrolyte content

began to be expelled from clays. Thus, with relatively unconsolidated sediment and moderate electrolyte content, squeezing at pressures up to 124 MPa does not significantly affect to the solution concentrations.

The membrane or filtering effect has been reported to be negligible by Manheim (1966) and Manheim and Bischoff (1969). Others found that there is a dependency between the pore water concentration and the squeezing pressure if the soils are saturated with monovalent ions (Lutz and Kemper, 1959). Von Engelhardt and Gaida (1963), and Chilingarian et al. (1973) found that in seawater-saturated pure montmorillonite, squeezed pore water concentration decreased with increasing pressures (from 3 to 386 MPa), which doesn't occur with kaolinite samples. Chilingarian and Rieke (1968) found that, depending on the type of clay, oriented water begins to be squeezed out in the range of pressures from 0.3 to 6.9 MPa. However, Rosebaum (1976) didn't find ion concentration changes at squeezed pressures between 0.98 and 29 MPa in samples from Lower Cretaceous of Nutfiel (UK), which consist mainly of calcium montmorillonite. Morgenstern and Balasubramanian (1980) and Iyer (1990) extracted the pore water from overconsolidated clays and clay shales from Canada (marine deposits from Upper Cretaceous: 19-32% w.c.) at squeezing pressures ranging from 4.8 and 52 MPa, founding that the chemical composition depended on pressure due to the mixing of free pore water and adsorbed water, but a threshold squeezing pressure could be established for avoiding this problem (5-20 MPa).

The British Geological Survey (BGS), performed different pore water studies with Oxford Clay (Cretaceous-Jurassic mudrock) at the Harwell Research Site (Brightman et al., 1985); and from glacial tills and Mesozoic (London Clay) and Tertiary mudstones (Entwistle et al., 1989; Entwistle and Reeder, 1993). In these works they found that this sampling technique produces very reproducible results to extract pore fluid and representative of *in situ* pore water for most chemical species, concluding that squeezing is the only practical way of physically extracting pore-fluid for geochemical analysis from low permeability clays and mudstones with low water contents (7-20%). They found chemical fractionation with increasing pressure of ions in some samples, decreasing monovalent cations and increasing sulfate and the divalent and trivalent cations, and smooth concentration profiles across the formation for the more conservative species, especially chloride. However, the chemical changes with pressure were probably due to possible contamination of the squeezer, oxidation of samples, reduction in moisture content and pore size, although anion exclusion processes was also pointed out.

In general, from studies performed in Underground Research Laboratories (URL): Mont Terri (1996, Switzerland), Meuse-Haute-Marne (1994, Bure, France) and HADES (1974, Belgium), squeezed pore waters were found to be representative of those from these argillaceous formations because they were comparable and similar with water *in situ* measurements obtained from piezometers and packered boreholes if they are obtained at squeezing pressures below a threshold value, specific for each formation: 30-35 MPa for the Tertiary plastic and consolidated Boom Clay at Hades (De Craen *et al.*, 2004), 150 MPa for the Jurassic indurated Callovo-Oxfordian formation at Bure (Fernández et al., 2009); and 175 MPa for the Jurassic indurated Opalinus Clay at Mont Terri (Pearson et al., 2003).

In clayrock formations with very low water content (1 to 4%) and high degree of induration, such as the Toarcian and Domercian clay formations at Tournemire (France), with a water content of 3.5% (6-9% porosity); or the Boda Claystone (Hungary) with water content of 2.1% (5.4% porosity), the squeezing technique was not possible to use for the extraction of the pore water (Michelot et al., 1995; De Windt et al., 1998; Fernandez et al., 2009), at least at squeezing pressures below 500 MPa.

In the thermo-hydro behaviour of bentonites as buffer and swelling material, squeezing technique was also used for pore water chemistry studies at different dry densities and solid to liquid ratios. Pore water chemistry from the MX-80 bentonite was analysed at VTT laboratory at Finland (Muurinen and Lehtikoinen, 1999), whereas Febex bentonite was analysed in CIEMAT laboratories at Spain (Fernández et al., 2001; Fernández and Villar, 2010). A chemical fractionation with increasing pressure was observed in these studies.

From all these works mentioned above, it can be concluded that validity of the squeezing technique depends on the experimental conditions and the type of the clay minerals (see for example Figure 6) and their properties. Perhaps, the most physicochemically unique feature of clayey sediments as

chemically reacting system is the manifestation of net negative charge by the clay mineral surfaces (cation-exchange phenomena). The range of cation-exchange capacity differs for each type of clay: kaolinite (3-15 meq/100g), illite (20-50 meq/100g), chlorite (10-40 meq/100g), montmorillonite (80-120 meq/100g). Burial compaction directly affects the porosity, water content and the density of clays and, therefore, the concentration of negative sites per unit volume is pressure-dependent. For comparison, a clay mud has a porosity of 70-90%, a soft clay and a compact clay (both present at shallow burial stage of diagenesis) have a porosity of 40-80% and 25-40%, respectively; a mudstone or a shale between 20 and 7%, whereas an argillite between 7 and 4%.

Depending on the specific surface area (illite and chlorite: 80 m²/g, kaolinite: 15-30 g/m², montmorillonite: 600-800 m²/g;) and electrical charge, the amount and the strength of water molecules adsorbed on the exposed surfaces of clay particles will be different. Therefore, different pressures would be needed to mobilise or remove the water from them (see for example Figure 7). The accumulation of counter charge by a clay particle or surface in order to maintain electrical neutrality leads to a differential distribution of anions and cations in the surrounding pore solution. This effect may be described from Donnan equilibrium, but it is more completely defined on the basis of the double-layer theory. Solutes in the aqueous phase may be associated with different types of waters: immobile water in the micropores, bound water at the clay mineral surfaces (immobile), and free (mobile) water flowing through meso-, macro-pores, depending of the distance to the net negative charge of the clay mineral surface.

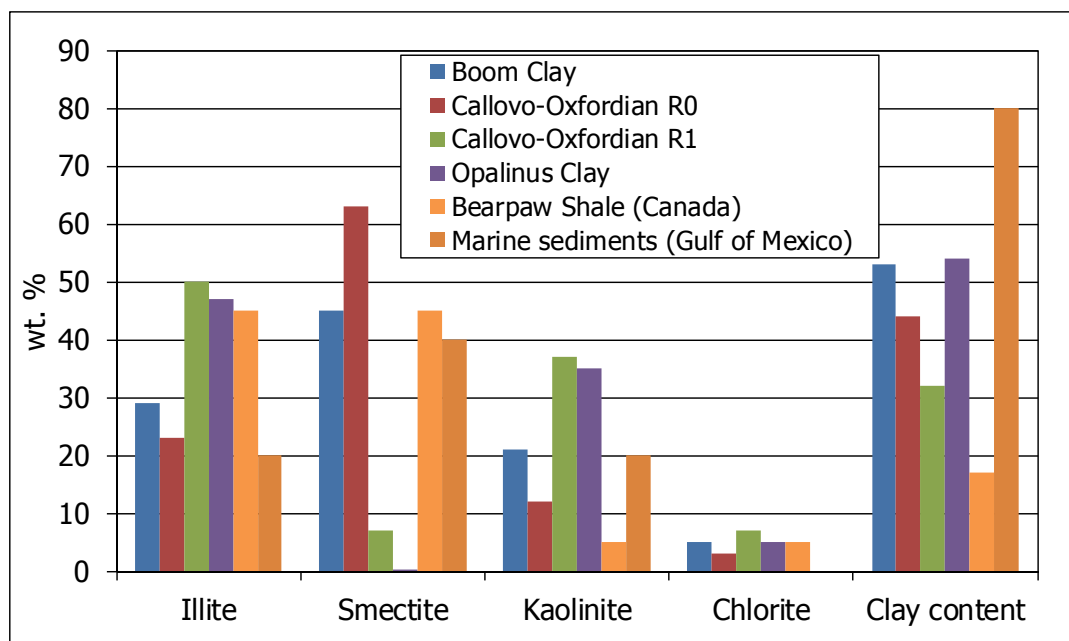


Figure 6. Variation of the clay content and type of clay minerals in different argillaceous formations (Data from: Iyer, 1990, Fernández et al., 2009; Manheim and Bischoff, 1969)

The water adsorbed on the surfaces of clay minerals has properties (water density and viscosity) that differ from those of ordinary liquid water because it exists in a force field. Indeed, some works indicate that Darcy equation describing the water flow in a porous media can not be applied to clays because part of the water is immobile or has a high viscosity (Low, 1976). At high water contents (or high porosities), in which the particles are relatively far apart, the release of water is easier because it is controlled by double-layer repulsion (osmotic swelling); whereas at low content contents or low porosities, in which particles are separated by only a few monomolecular layers of water; the forces of adsorption of the water layers on the clay surfaces controls the water desorption process. In all cases, water desorption is enhanced by the effect of temperature.

Besides, due to the negatively charged framework of the clay material (i.e., ion-exchange capacity), shales and compacted clay minerals are capable of acting as ion excluders, i.e., behave as semi-permeable membranes, which retard or prevent the passage of charged ionic species through the membrane pores while allowing relatively free movement of uncharged species. This phenomenon is termed, salt filtering, reverse osmosis, filtration effect or ultrafiltration. As result of ion-exclusion, the effluent (ultrafiltrate) is less concentrated than the original solution (Hanshaw and Coplen, 1973).

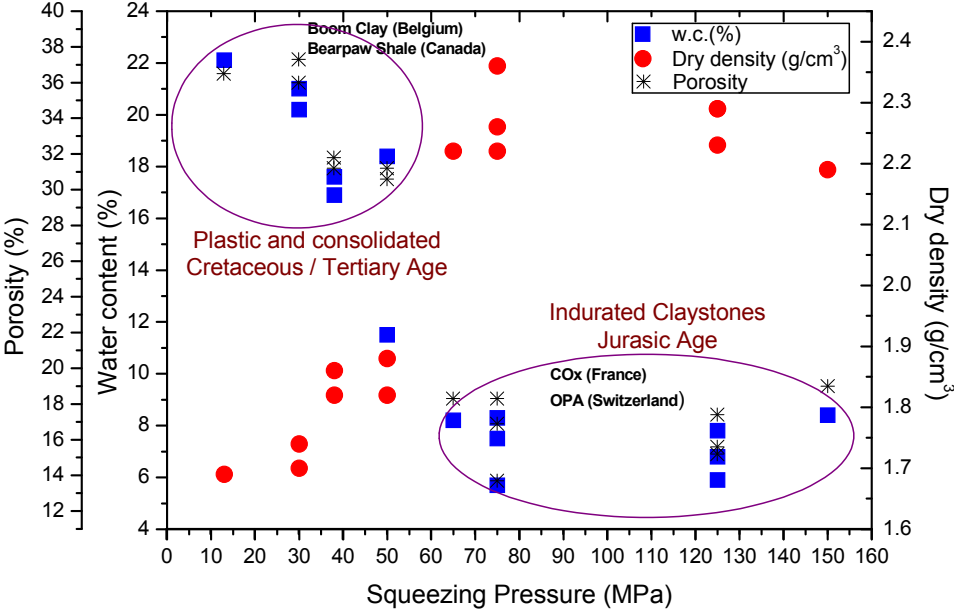


Figure 7. Squeezing pressures needed for pore water extraction as a function of water content and dry density of the core samples in different formations

It seems that a good practice for obtaining a representative pore water sample of homogeneously distributed electrolytes in the bulk aqueous phase, implies to avoid the sampling different proportions of the DDL water. The greater the squeezing pressure, the greater the ease with which strongly-bound water around particle surfaces is expelled. Therefore, the strength of the pressure to be applied for extracting only the free pore water must be determined previously for each clayey material. This strength influencing the water removal and particle is going to depend on different physico-chemical factors such as porosity and pore size distribution, the water content type of clay minerals.

5.2. *Reproducibility of squeezed waters: Comparison of results obtained from other squeezing tests and with the water-extraction method (aqueous extracts tests)*

The reliability of an squeezed water, in terms of how representative is of an *in situ* pore water, depends on various factors concerning the rock sample itself, as well as, the experimental conditions and procedures used for squeezing. A first procedure to validate a method for extracting pore water is to check the reproducibility of the data with the same technique. Another one is compare quantitatively results obtained with another method, such as *in situ* tests and aqueous leaching.

5.2.1. *Comparison of squeezing tests from different laboratories*

In Figure 8, the comparison of the squeezed pore waters obtained by different laboratories: BGS (UK) and CIEMAT (Spain) is shown. In these squeezing tests, the subsequent core samples belonging to same borehole (BWS-E4, BWS-A6 and BWS-E6) were analysed. It is worthy to note here that BGS tests were performed by using a one directional fluid flow, thermoregulated and anaerobic system (~ 4

ppm O₂), keeping the temperature at 10 ± 2°C and a 316 stainless steel squeezer 75 mm diameter and 100 mm high; whereas CIEMAT used a two directional fluid flow system at ambient conditions with a 329 stainless steel squeezer 70 mm diameter and 500 mm high. The mass used at both labs ranged from 624 g to 737 g at BGS and between 1500 g and 1600 g at CIEMAT.

A global view of the data indicates that, although different squeezing pressures were used at both labs (fixed at 70 MPa at BGS and non-fixed at CIEMAT), the technique is quite reproducible. For the conservative elements such as chloride and bromide, the concentrations are similar, with differences for chloride of less than 7%, taking into account the dilution of the water sample extracted (between 2 and 3 mL at BGS and 2 and 5 mL at CIEMAT). The higher amount of squeezed water were obtained both at BSG and CIEMAT, 5 and 3.23 mL, respectively, in the core sample BWS-E6; and the lower amount of water, 2 and 2.82 mL, respectively, were obtained in the core sample BWS-E4. The difference of extracted water obtained from the different core samples is more related with the initial water content than with the Facies of the Opalinus Clay. Initial water contents were 7.1% (BGS) - 7.8% (CIEMAT) for the BWS-A6, 6.4% for the BWS-E6 (Jurensis Marl) and BWS-E4 (Sandy Facies) core samples, respectively. In the Shaly facies of the Opalinus Clay (BWS-A6 cores), the initial water content ranged between 7.2% (BGS) and 7% (CIEMAT); being 2.68 mL (BGS) and 3 mL (CIEMAT) the squeezed water.

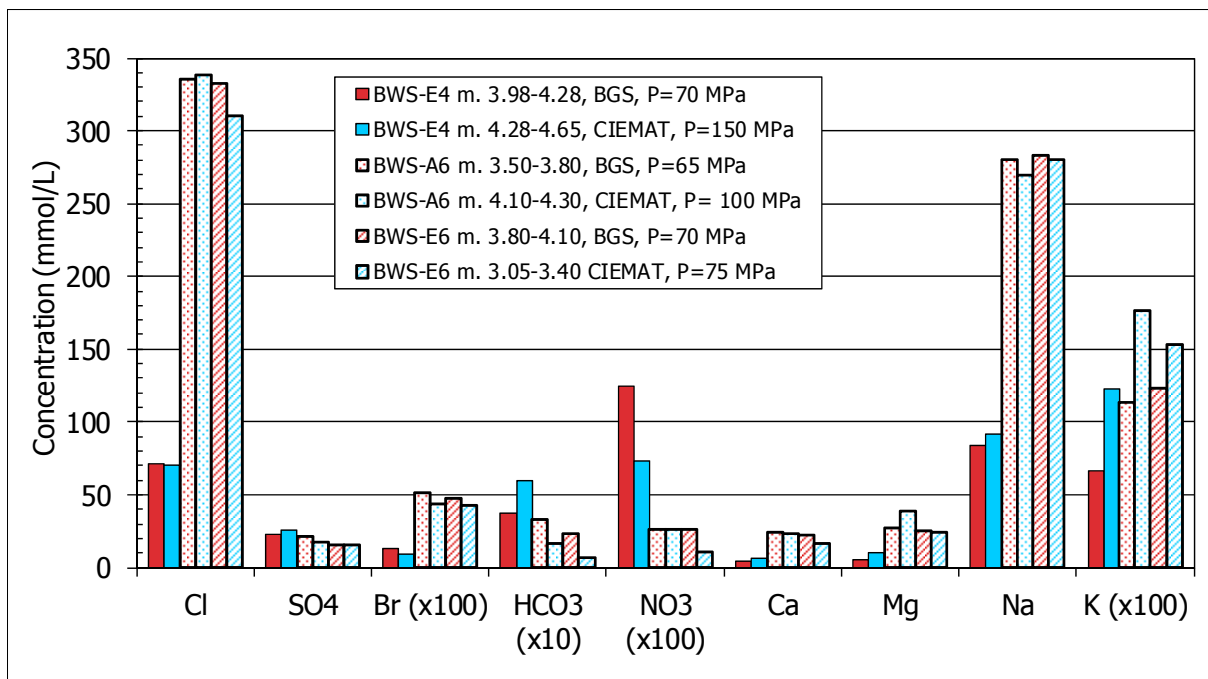


Figure 8. Comparison of ion content obtained by squeezing at different pressures in BGS and CIEMAT laboratories

Dilution of the water samples are necessary for ion chromatography technique due to the high salinity of this type of pore waters (I=0.41-0.14 M). However, it is interesting to say that thanks to this high salinity, the 2-3 mL water samples extracted can be diluted to a final volume of around 20-25 mL for performing a complete chemical analysis of the pore water. On the other hand, due to the high amount of chloride and that the bromide and chloride peaks are quite close in a chromatogram, the bromide concentration must be carefully determined or by using an specific column that separate both concentration peaks.

Regarding to non-conservative anion species, sulphate concentrations are quite similar, the variations in bicarbonate and nitrate concentrations being higher. However, these variations are not systematic and change from one core sample to another and from lab to lab. Therefore, they cannot be attributed to a temperature effect during the water extraction which is different for both labs, or to an increase of

the carbonate solubility due to pressure (squeezing pressures were different at BGS and CIEMAT labs), but to a slight oxidation process during the squeezing tests. The higher the sulfate and/or nitrate concentrations the more bicarbonate content, increasing also calcium and magnesium. Sodium differences range between 0.8 to 9.4% probably related to exchange reactions at clay mineral surfaces after the oxidation process. The presence of nitrate in some waters indicates a possible oxidation of ammonium species probably absorbed onto clay exchange sites as it was detected in core samples from borehole BWS-A6 (Waber et al., 2003). Ammonium ion has a high ion exchange selectivity. Other sources of nitrate may be the oxidation of ammonia liberated by the breakdown of organic matter.

The variations in potassium concentrations are much higher and between 24% and 84%. Systematically, potassium concentrations at CIEMAT are higher than those from BGS. One explanation can be related to the temperature effect during squeezing. At BGS the squeezing test is thermoregulated at 10°C whereas at CIEMAT is at laboratory conditions of 22°-25°C. Potassium enrichments (13.3%) are described in literature by warming of marine sediments by raising the temperature about 20°C during core sampling and squeezing (Manhelschhof et al., 1969; Bischoff et al., 1970; Fanning and Pilson; 1971; Sayles et al., 1973; Gieskes, 1975); and they are due to changes in ion-exchange selectivity as a function of temperature. However, most of these changes seem to be completely reversible on re-equilibration and storage of the core samples at *in situ* temperatures or performing the squeezing tests by using thermoregulation (Kalil and Goldhaber, 1973; Masuzakada et al., 1980).

It is worthy to note that the total efficiencies of the extractions at both labs were different. For BGS the total efficiencies (extracted water vs. total water in the sample) were of 22%, 21% and 10% on samples BWS-E4, BWS-A6 and BWS-E6, respectively; whereas at CIEMAT were of 12%, 12% and 17% on the same samples respectively. The difference is in the applied squeezing pressure being of 70 MPa for all samples at BGS and 150 MPa, 100 MPa and 75 MPa in samples BWS-E4, BWS-A6 and BWS-E6, respectively, at CIEMAT. Therefore, increased pressure seems to affect to the permeability of the material due to decrease of pore sizes. However, the chemistry of the pore water does not change with pressure.

Both at BGS and CIEMAT studies, there is no an indication of contamination of the pore water by corrosion of the metal of the cell and the sintered filters. Values of chromium and nickel are usually below detection limits in the pore water samples.

5.2.2. Comparison between squeezing and aqueous leaching data

A direct comparison of squeezing results with aqueous extract or aqueous leaching tests is not possible because in leaching tests water is added in excess with respect the natural one, which changes the solubilities of certain mineral phases from the clayrock (carbonates, sulfates, etc.). In aqueous extracts, dilution of species in the pore water as well as dissolution of minerals occur and, therefore, the concentration of anions, as well as cations (via dissolution and exchange reactions) changes as a function of the solid to liquid ratio employed. For this reason, the ion concentration in squeezed pore water is higher than those determined by using aqueous leaching. Aqueous leaching are carried out at low solid to liquid ratios and the unconstrained dissolution of highly soluble salts and sparingly soluble minerals, together with cation exchange reactions on the clay minerals, leads to pore water compositions and cation occupancies which are far away from the *in situ* conditions. Indeed, the chemical composition in an aqueous extract is the sum of: a) the constituents originally dissolved in the real pore water, b) the mineral dissolution reactions during the leaching process as a function of the amount of water used, c) any constituents contributed from cracked fluid inclusions, and d) cation-exchange reactions, which affect the exchanger population of clays.

In an aqueous extraction test, the concentration of a chemically conservative component that has only one source (i.e. the pore water) will show a linear behaviour as a function of the solid to liquid (S:L) ratio used in the extractions tests, and will have a zero-concentration intercept at a S:L ratio of 0

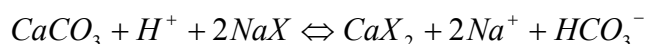
(infinite dilution). A linear trend is produced if a solid phase dissolves kinetically, whereby the contribution from the dissolving solid is proportional to the rock mass (i.e., proportional to the S:L ratio). If the adequate geochemical porosity for such component is known, its concentration in the aqueous extract solution at a specific S:L ratio can be converted into the real *in situ* pore water concentration (Bradbury and Baeyens, 1998).

In the rock samples analysed, the pH and the concentration of ions in the aqueous extracts depended of the solid to liquid ratio. pH decreased with increasing S:L ratio, whereas the ion concentration increased as the amount of water implied in each test increased with the S:L ratio. This general behaviour can be clearly observed in the tests performed on the BHT-1 core sample (Figure 9 and Figure 10). Chloride and bromide show a linear behaviour at different S:L ratios (Figure 9). Their concentrations correlate linearly with the S:L ratio with a zero intercept for all samples, which suggests that under *in situ* conditions all Cl⁻ and Br⁻ are in solution and originates from the pore water.

SO₄²⁻ seems to follow also a linear trend in S:L versus concentration, but SO₄²⁻ from an aqueous leaching may only be directly converted to pore water concentrations if pyrite oxidation is avoided, or if other source of soluble sulphate is not present (gypsum, celestite, ...). In the case of the Opalinus Clay formation, gypsum could be a secondary alteration product induced by the pyrite oxidation. The sulphate content in the pore waters of the Opalinus Clay should be limited by the SO₄/Cl ratio of seawater (upper limit), due to its marine origin. For this reason, any value of sulphate above this ratio can be considered as a product of the oxidation of the pyrite (Pearson et al., 2003; 2011).

A non-linear trend was observed for HCO₃⁻, which implies that a soluble salt is dissolving to its solubility limit at each S:L ratio. It is expected to dissolve some carbonates (calcite, dolomite) present in the Opalinus Clay. This dissolution affected the pH and cation concentration values, which decreased and increased, respectively; following a non-linear relationship when the S:L ratio increased (Figure 10). This is due to ion exchange reactions provoked by carbonates dissolution.

At low S:L ratios, when the amount of water increases, the calcium (and Mg) liberated due to the calcite (or carbonates) dissolution, interchanges with the sodium of the interlayers. As a consequence, the sodium (and K) concentration in solution increase, and the calcium and Mg concentrations remain constant or slightly increase in the aqueous extracts solutions (Figure 10). These processes are supported by the following dissolution-exchange reaction, which implies the observed pH decrease when the S:L ratio increased:



The whole of results indicate that in addition to the dissolution/precipitation reactions, the cation exchange reactions must play a fundamental role in the pore water chemistry. Here, it is interesting to note that important efforts were made in the context of Mont Terri Project to determine accurately the CEC and exchangeable cations (Waber et al., 2003). CEC and cation exchange population from the cores analysed in this work are shown in Table 5. After the tests over time, it was concluded that for avoiding or limiting problems both with carbonates dissolution and pyrite oxidation, the tests must be performed at a relatively high solid to liquid ratio (1:4, 1:8), by using a reduced sample-solution contact time (30 min-1 hour) and performing the tests inside an anoxic glove box.

As conclusion, only the concentrations of Cl⁻ and Br⁻ in the aqueous extract solutions can be directly converted to pore water concentrations provided that no Cl- and Br-bearing salts are present in the rock under *in situ* conditions. Therefore, the comparison between aqueous leaching and squeezing pore water composition could be only performed for conservative anions, such as chloride and bromide (i.e., for species that follows a linear relationship ion concentration versus S:L ratio as in Figure 9), when the extracts are extrapolated or calculated to the amount of free or external water, not to the total water or moisture content of the clayrock. Extrapolations of pore water concentrations at the natural moisture content of the clayrock from the concentration of a diluted aqueous extract solution result in an overestimation of the pore water salinity, because non-conservative ions concentration increases in these extracts due to mineral phase dissolution and exchange reactions (Bradbury and Baeyens, 1998; Iyer, 1990; Devine et al, 1973; Pearson et al., 2003). The total water content is usually known by drying the clayrock at 150-200°C (not to 110°C) as it is observed by

thermogravimetric analysis (TG). The problem is to ascertain the amount of water not involved at exchange sites and at double layers, i.e., to know the amount of free water or external water, which is available for solute transport.

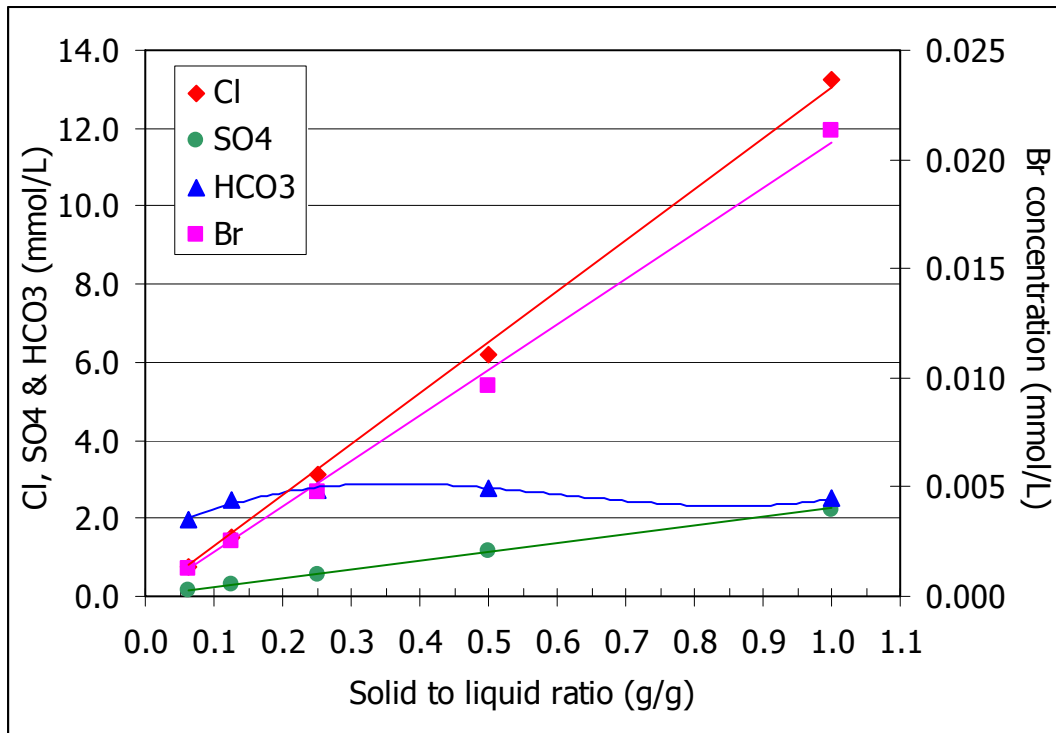


Figure 9. Anion concentration (mmol/L) in an aqueous extract solution as a function of the solid to liquid ratio on the core sample BHT-1. The analytical error is $\pm 5-10\%$

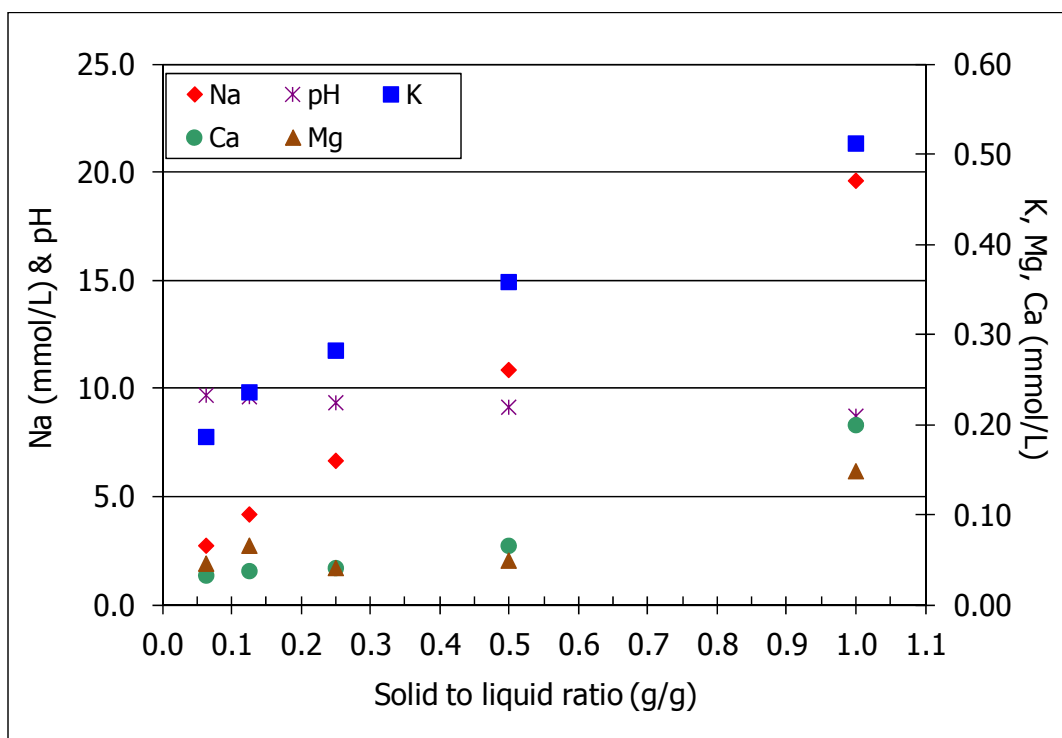


Figure 10. Cation concentration (mmol/100g) in an aqueous extract solution as a function of the solid to liquid ratio on the core sample BHT-1. The analytical error is $\pm 5-10\%$

The anion inventories for all core samples were determined from the aqueous leaching tests (Table 10). The data were calculated as an average from all solid to liquid ratios available because not large variations were observed, except for the BHT-1 and BDR-2 core samples. In these latter cores the data obtained at 1:8 and 1:16 solid to liquid ratio were only used because at these low solid to liquid ratios a complete extraction of salts was obtained.

The chloride inventory decreases as a function of the distance towards the overlain Dogger Limestone formation, as expected to the evolution of the pore water in the Opalinus Clay formation (Pearson et al., 2003). However, sulfate inventories do not follow a clear tendency because they are affected by kinetically controlled processes of pyrite oxidation. The higher oxidation process the higher sulphate inventory, which is observed in the samples BWS-A4 and BWS-A5 whose aqueous leaching tests were performed outside an anoxic glove box. The use of an anoxic glove box ($O_2 < 1$ ppm) for performing aqueous leaching tests (BHT-1 and BDR-2 samples) with boiled and des-aired deionized water, limits the extent of a possible oxidation of pyrite during leaching tests, but there is no any guaranty of a possible oxidation during core sample handling and storage (Tournassat et al., 2008; Gaucher et al., 2009).

Table 10. Anion inventories obtained from leaching tests for different core samples from Opalinus Clay

Anion	Cl ⁻ (mmol/kg)	Br ⁻ (mmol/kg)	SO ₄ ²⁻ (mmol/kg)	SO ₄ ²⁻ /Cl ⁻ ⁽¹⁾	Br ⁻ /Cl ⁻ ⁽¹⁾
BWS-E6 m. 3.05-3.40	15.51 ± 0.08	0.019	13.10 ± 0.50	0.84	0.0012
BWS-A6 m. 4.10-4.30	12.41 ± 0.16	0.018	8.08 ± 0.24	0.65	0.0015
BWS-A4 m. 6.99-9.94	15.42 ± 0.96	< d.l.	18.10 ± 6.00	1.17	--
BWS-A5 m. 7.40-7.79	11.57 ± 0.58	< d.l.	14.46 ± 0.80	1.25	--
BHT-1 m. 12.4-12.9	11.83 ± 0.17	0.019	2.33 ± 0.01	0.20	0.0016
BDR-2 m. 5.93-6.36	6.88 ± 0.16	0.010	1.39 ± 0.03	0.20	0.0015
BWS-E4 m. 4.28-4.65	1.97 ± 0.01	< d.l.	4.23 ± 0.03	2.15	--

⁽¹⁾Seawater molar relationship: $SO_4^{2-}/Cl^- = 0.05$; $Br^-/Cl^- = 0.0015$

5.3. Reliability and representativity of squeezed waters: Comparison with borehole water data

Demonstrating the veracity of a technique for obtaining “true” pore water solution is problematic because direct measurement of pore water composition may be impossible. In the context of the Mont Terri Project, different tests have been performed for obtaining *in situ* water from packered-off boreholes (Pearson et al., 2003). This allowed us a direct assessment of whether pore water chemistry obtained by squeezing represents the real or original water chemistry by simple comparison of both type of pore waters.

The chloride concentration of squeezed and *in situ* borehole waters can be seen in Figure 11. Squeezed waters follow the same trend than borehole waters obtained from Opalinus Clay across the NW-SE section at Mont Terri Rock Laboratory. Besides, both show the same water-type and salinity. The chemical composition of the squeezed pore waters are Na-Cl water-type with an ionic strength ranging between 0.14 M and 0.43 M, in agreement with the variation of the salinity observed at *in situ* conditions in borehole waters. Chloride concentration profile in the pore waters decrease towards the Lower Dogger formation, being the higher concentration located in the borehole BWS-A6 (12 g/L). Lower chloride content is also found in the borehole BWS-E6 (11 g/L) located in the Liassic Jurensis Marl formation where a sharp concentration drop is observed. The pore water from the core sample BHT-1 has an ionic strength of 0.34 M, pH 7.7 and a chloride concentration of about 10 g/L, which is similar to the *in situ* seeping water obtained from borehole BWS-A1 located in the Shaly facies of the Opalinus Clay (Pearson et al., 2003), which is considered as the reference water type of the Opalinus Clay formation. The squeezed water from the core sample BDR-2 is Na-Cl type with an ionic strength

of 0.21 M, pH 7.3 and chloride concentration of 6.1 g/L, which is similar to *in situ* waters obtained in the borehole BWS-A3 located in the Shaly/Sandy facies of the Opalinus Clay. The lowest chloride content is found in the borehole BWS-E4 (2.5 g/L) which located close to the Dogger Limestones. Furthermore, the squeezed pore water from the core sample BHT-1 could be compared with an *in situ* seeping water from this borehole (Table 11). The comparison between of compositions from both extracted waters is good, although slight differences were observed for pH and sulphate, silica and potassium concentrations. However, these deviations are due to artifacts during extraction, which can be corrected as we will see later. Therefore, the squeezed water can reproduce the chemistry of the *in situ* pore water regarding ionic strength and chloride concentration (Figure 11). The Cl concentration versus the location of the boreholes in the underground laboratory in a NW-SE profile, depicts a trend that seems to indicate an effect of solute transport. The lower content of the chloride in Opalinus Clay at both boundaries seems to be related to a diffusion mechanism from the Opalinus Clay towards the overlying (Lower Dogger limestones) and underlying formations (Jurensis Marls). The Lower Dogger is a recharge and karstic zone containing dilute meteoric water, which establishes a chemical gradient in relation to the clay formation with high saline contents. This leads to a long-term large-scale process of mass transfer by diffusion (Pearson et al., 2003, Mazurek et al., 2011).

Table 11. Comparison between the *in situ* BHT-1 borehole water and the squeezed water obtained at 75 MPa

Parameters	pH	Cl ⁻ (mg/L)	Br ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Alkalinity (meq/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Sr (mg/L)	Si (mg/L)	δ ¹⁸ O (‰)	δ ² H (‰)
Borehole water	7.12	9730	36.4	1470	2.32	5470	82.3	643	469	40.1	5.34	-8.53 ± 0.14	-53.07 ± 0.96
Squeezed water	7.70	9800	30.0	1700	1.82	5400	55	673	540	45	3.20	-8.11	-53.5

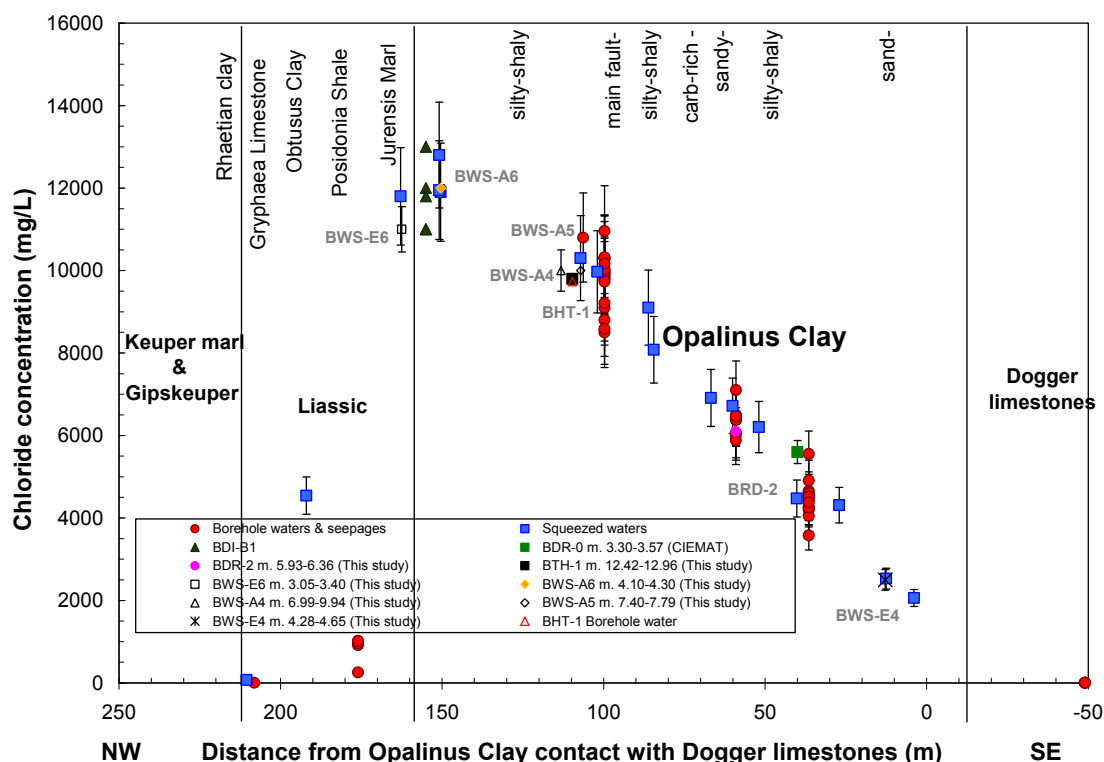


Figure 11. NW-SE cross-section of chloride concentrations in waters from Mont Terri and comparison with the squeezed waters (after Pearson et al., 2003)

Stable isotope analyses were only possible on the BHT-1 core sample, after performing a duplicate squeezing test due to volume limitations for both chemical and isotopic analysis. Stable isotopic composition requires at least 2 mL of water for the analysis. Comparison of squeezed and *in situ* borehole waters for stable isotopic data, $\delta^{18}\text{O}$ and $\delta^2\text{H}$, is shown in Table 11. Data ranged between -8.11 and -8.53 ‰ for $\delta^{18}\text{O}$ and -53.1 and -53.5 ‰ for $\delta^2\text{H}$ on the Standard Mean Ocean Water (SMOW) scale which seems to indicate that no isotopic fractionation occurs during squeezing when analytical uncertainties are taken into account. The fluctuations are possible due to problems in handling small samples. Indeed, squeezed waters follow the same trend that *in situ* borehole data (Pearson et al., 2003) as can be seen in Figure 12. Isotopic data decrease steadily when approaching to the Dogger Limestones showing values that tend to typical of depleted meteoric waters involved in recharge, whereas pore water with higher salinity shift towards heavier values tending towards that of sea-water (0 ‰ $\delta^{18}\text{O}$ and $\delta^2\text{H}$), which is normally interpreted as evidence for older waters.

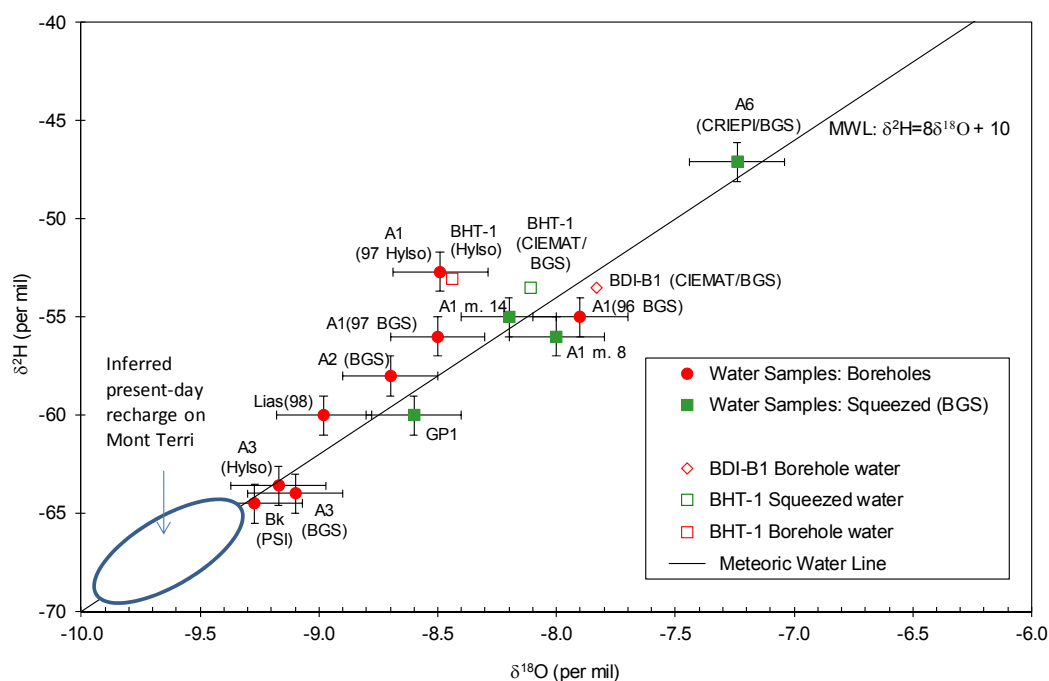


Figure 12. $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ in squeezed BHT-1 sample and their comparison with data from borehole waters and pore waters in drillcores obtained at Mont Terri (after Pearson et al., 2003)

Different parameters of the pore waters analysed were calculated in order to check the analytical composition of the squeezed pore waters (Table 12). Some parameters are usual relationships, such as charge balance, or the SO_4/Cl and Br/Cl ratios. Other ones are related to mineral saturation indexes, pCO_2 , etc., which were obtained with the Phreeqc program (Parkhurst and Appelo, 1999) and the Thermoddem database (BRGM, 2011).

The charge balance of all the squeezed water is below 5%, which indicate a good chemical analysis despite the small amount of water extracted (1-5.5 mL) and its dilution for analysis. The Br/Cl molar ratio is similar to the seawater ratio (0.0015 molar), which was observed in all *in situ* borehole waters from Mont Terri. This ratio suggests a syndimentary marine origin of the pore water, although the Cl and Br concentrations are lower than the seawater values (~half of the seawater values). The lower Br/Cl ratio obtained in the sample BWS-A6 (0.0013 molar ratio), maybe related to the analytical error in the bromide concentration obtained by IC when a separate column is not used in the analytical system. This allows to discriminate the bromide and chloride peaks in the chromatogram when waters having a high chloride content are being analysed. Actually, most of the laboratories have this separate column.

The SO_4/Cl molar ratio of the pore waters is close to that of the seawater (0.05 molar) in the samples BWS-E6, BWS-A6, BHT-1 and BDR-2, as occurred in non-oxidised *in situ* borehole waters from Opalinus Clay at Mont Terri (Figure 13). Large variations with respect to this SO_4/Cl ratio is observed in the samples BWS-A4, BWS-A5 and BWS-E4 (Table 12), whose sulfate concentrations are very high. The sulphate concentration in Opalinus Clay pore waters are regulated by the SO_4/Cl ratio of seawater due to its marine origin (Pearson et al., 2003). For this reason, any sulphate value above this ratio can be considered as product of the pyrites oxidation contained in the clayrock (~1.1%). Therefore, in these core samples an oxidation of the core sample occurred. However, it is difficult to elucidate if this oxidation occurred during sampling, manipulation, transport, storage, handling or during the squeezing test. The presence of nitrate in some waters indicates also some kind of oxidation of the core samples.

The redox values in a squeezing test is not possible to be measured in an accurately way. For this reason, the Eh valued only can be obtained by geochemical modelling. In the case of Opalinus Clay pore waters, Eh can be calculated according to the pyrite/ SO_4 redox couple (Pearson et al., 2003) at the pH measured, which ranged between -158 to -243 mV.

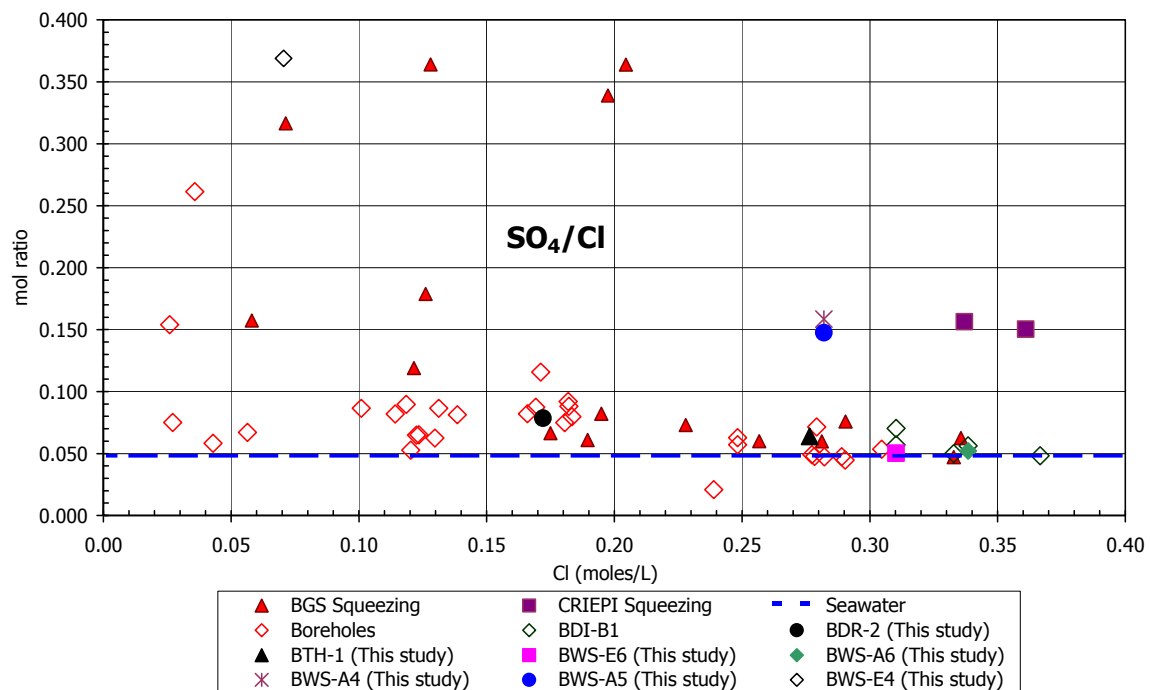


Figure 13. Comparison of SO_4/Cl molar ratios of waters from Opalinus Clay at Mont Terri and the squeezed waters obtained in this study (after Pearson et al., 2003)

5.4. Saturation index of mineral phases

The squeezed pore water should be at equilibrium with the mineral phases present in the Opalinus Clay rock (see section 3.1). Deviations from this equilibrium may be checked by the saturation index of the mineral phases (Table 12).

Table 12. Evaluation of the parameters yielded for the data sets analysed (lab conditions 22°C)

Evaluation parameter	Charge balance	SO ₄ /Cl	Br/Cl	pH Lab	SI calcite	pH corrected ^(1,3)	SI ⁽²⁾ calcite	SI ⁽²⁾ dolomite disordered	SI ⁽²⁾ strontianite	SI ^(2,3) quartz	pCO ₂ ⁽²⁾ calculated	SI celestite
BWS-E6 75 MPa	3.49	0.050	0.0014	6.8	-0.86	7.679 (7.790)	0.0	-0.51	-0.73	--	-3.28	-0.04
BWS-A6 100 MPa	2.99	0.052	0.0013	6.9	-0.26	7.160 (7.233)	0.0	-0.45	-0.83	--	-2.38	-0.03
BWS-A4 88 MPa	4.54	0.167	0.0015	7.2	--	--	--	--	--	--	--	0.39
BWS-A5 125 MPa	-2.87	0.170	0.0015	7.6	--	--	--	--	--	--	--	0.34
BHT-1 75 MPa	0.42	0.064	0.0014	7.7	0.47	7.210 (7.278)	0.0	-0.55	-0.73	-0.15 (-0.03)	-2.35	0.06
BDR-2 125 MPa	-2.91	0.079	0.0014	7.3	-0.08	7.386 (7.536)	0.0	-0.72	-0.52	-0.38 (-0.27)	-2.59	0.17
BWS-E4 150 MPa	-0.84	0.369	0.0012	8.1	0.98	7.080 (7.140)	0.0	-0.38	-0.26	--	-1.64	0.47

(1) If SI calcite > 0 then pH_{corrected} = pH - SI_{calcite}

(2) Saturation index and pCO₂ calculated with corrected pH values

(3) in parenthesis: pH and SI of quartz calculated at temperature *in situ* conditions of 13°C after pH correction

As expected, squeezed pore waters are at equilibrium or oversaturated with respect to Celestine. According to the mineralogy, Opalinus Clay pore waters should be at equilibrium with carbonates. BDR-2 pore water is at equilibrium with calcite, whereas pore waters are oversaturated and unsaturated with respect to this mineral for BHT-1 and BWS-E4 and for the rest of squeezed waters, respectively. Therefore, different processes are affecting the pore waters. Oversaturation of calcite is mainly due to a CO₂ degassing process during water extraction, which affects to the pH and TIC values of the pore waters, increasing and decreasing both values, respectively. This can be seen in waters from borehole BHT-1, in which squeezed pore water pH is higher than that obtained *in situ* (Table 11).

This deviation can be correct by using the geochemical equilibrium Phreeqc program adjusting the pH at calcite saturation. This affects to the alkalinity-pH-CO₂ system, for what new values for pH and saturation index for calcite, dolomite, strontianite and PCO₂ were obtained (see Table 11). Now the pore waters are saturated with respect to calcite, and with a lower pH (except if the initial SI calcite was undersaturated). The corrected values for the SI of dolomite and strontianite indicate undersaturation; and the log partial pressure of CO₂ ranged between -3.28 to -1.64 atm (Table 12). These last values are far away from the atmospheric Log pCO₂ (-3.5 atm). On the other hand, it is interesting to note that the alkalinity values are low, indicating that no bacterial activity is produced during the squeezing test. An increase of pH after calcite saturation indicates a possible oxidation of the squeezed pore waters. This is observed in BWS-E6 and BWS-A6 core samples. In the BHT-1 squeezed pore water where it is evident a slight oxidation process according to its comparison with the *in situ* borehole water (higher pH and sulphate and lower alkalinity), the SI calcite is oversaturated because the degassing process is higher than the oxidation process. The difference in the collection of the squeezed pore waters is that BWS-E6 and BWS-A6 pore waters where collected inside a syringe,

whereas the BHT-1 pore water was collected inside a vacuum vial. This allowed the CO₂ ex-solution inside the dead volume of the sampling vial.

The low SiO₂ concentration in the pore waters as well as the mineralogy studies indicates that quartz controls the concentration of this specie. According to the SI saturation of quartz the pore waters are undersaturated with respect to this mineral, which disagrees with the natural occurrence in Opalinus Clay (Gaucher et al., 1993). This can be explained by a temperature effect, i.e., a slowness of re-equilibration at higher temperatures. The Operational temperatures of the squeezing tests were performed at laboratory conditions ($\sim 22 \pm 1^\circ\text{C}$), which is far away from the *in situ* conditions of $\sim 13^\circ\text{C}$. The change in the temperature of storing and extracting pore waters may affect to the nature of the water (see later), which can be observed in the saturation indexes of the some mineral phases. However, this effect is reversible and can be corrected by using the *in situ* temperatures during extraction (see section 5.2) or by geochemical equilibrium if the *in situ* temperature is considered in the calculations (Table 12). In this case, at a temperature of 13°C , the saturation index of quartz for BHT-1 sample is -0.03, which indicates equilibrium conditions with respect to that mineral phase.

5.5. Effects of pressure in extracted pore waters

Theoretically, an increase of pressure affects the mineral solution equilibria increasing the solubility of minerals (Langmuir, 1997). The effect of pressure on reactions involving only solid phases can be assumed to be negligible. However, when a gas is among the reactants, changes in pressure are generally important, and are enhanced by an increase of temperature. An accurate evaluation of the pressure effect on solubility requires data about molar volumes of reactants and products, due to mineral compressibilities can be considered negligible:

$$\left(\frac{\partial \Delta G_r^o}{\partial P}\right)_T = \Delta V_r^o \quad \text{Eq. 11} \quad \text{and} \quad \left(\frac{\partial \ln K_{eq}}{\partial P}\right)_T = \frac{\Delta V_r^o}{RT} \quad \text{Eq. 12}$$

where, ΔV_r^o is (cm^3/mol) the molar volume change of the reaction with all reactants and products in their standard states (Millero, 1982). This equation shows that the effect of a change in pressure on K_{eq} is proportional to the magnitude of the molar volume change of the reaction:

$$\ln \frac{K_p}{K_{1bar}} = -\frac{\Delta V_r^o (P-1)}{RT} + \frac{\Delta \bar{K}_r^o (P-1)^2}{2RT} \quad \text{Eq. 13}$$

where K_p and K_{1bar} are the equilibrium constant at P and the reference pressure, which is usually 1 bar; and \bar{K}_r^o is the standard partial molar compressibility ($\text{cm}^3/\text{mol}\cdot\text{bar}$). If ΔV_r^o is not a function of pressure, the second term of the above equation can be rejected.

Using this equation, the equilibrium constant for different minerals and species have been calculated from Thermoderm database for the squeezing pressures used in this work: water, bicarbonate, CO₂ (aq), calcite, dolomite, celestite, barite and halite. Tabulated values of ΔV_r^o for minerals were found in the Handbook of Chemistry and Physics (CRC Press, 1994), whereas for species in water and seawater were taken from Millero (1982). As result, only $\log K_p$ constants for bicarbonate and CO₂ (aq) species decrease with pressure, increasing for the rest of solid minerals and for water. This effect is much lower when salinity of the water increases (seawater). Therefore, the major effect of pressure is probably to cause gas to be dissolved into the pore water, mainly CO₂ gas. Thus, theoretically the effects of pressure should be only limited to the carbonate system.

Three tests were performed as a function of the squeezing tests for core samples BWS-A4, BWS-A5 and BHT-1. No water could be squeezed out at pressures lower than 75 MPa for this clayrock with water contents ranging between 6.2 and 7.8%. Two hypothesis were considered when the data as a function of pressure were evaluated: 1) if pressure involve the dissolution/dissociation of different phases, changes in the concentration of species would be observed, and 2) if the clays acts as a semipermeable membrane, ions can be excluded allowing only the pass through of fresher water

squeezed water (ultrafiltration phenomena). Thus, the water in the ion-excluding clays will become more concentrated and the squeezed water will be less concentrated in excluded ions. The efficiency of ion exclusion would increase with pressure, decreasing the squeezed pore water. In short, due to the mixture of the true pore water (free pore water) and the outer layers of the double-layer water, the concentrations would be change, decreasing the concentration with increasing pressure.

As can be seen in Figure 5 and Table 9, the ion concentration doesn't change with pressure, i.e., remained almost constant up to 200 MPa, with a slight variation in sulfate, alkalinity and potassium. However, these changes can be explained by other processes. Therefore, it seems that the true pore water is obtained at pressures up to 200 MPa in Opalinus Clay.

A water sample volume between 1 and 2.5 mL were extracted at each increased pressure for core sample BHT-1 (2 mL in borehole BWS-A4 and 3 mL in BWS-A5) for what the size of the flow channels has been maintained essentially the same at all squeezing pressures avoiding possible membrane (filtering effect). Therefore, the composition of the pore water was not dependent on the quantity of the water extracted and on the squeezing pressure up to 200 MPa.

The slight increase of sulfate concentration is related to an oxidation process of pyrites from the rock sample with increasing experimental time. This oxidation process was also evidenced by the increase of the SO_4/Cl molar ratio relationship, the decrease of pH and the increase of the NO_3^- concentration in the squeezed pore waters. This oxidation affected to potassium and alkalinity values, increasing bicarbonate content via the chain reactions: pyrite oxidation $\rightarrow \text{H}^+ \rightarrow$ calcite dissolution \rightarrow K-Ca ion exchange. However, this slight oxidation was produced mainly due to large experimental time and not because of increasing pressures, as it was confirmed in the squeezed pore water from borehole BWS-A6 where the test was performed at 100 MPa for 15 days, and the sulphate concentration was similar to that obtained in *in situ* seep waters with a SO_4/Cl molar ratio similar to seawater. Other tests performed in shorter time such as BWS-E4, BHT-1, and BDR-2 gave similar results. However, even in these tests is not clear that a slight oxidation did not take place in the core sample.

Due to the definition of squeezing, the pressure exerted in the squeezing cell acts on the gas and the water and it is negligible on the solid phases, so the pressure effects on dissolving minerals should be discarded. Therefore, the major effect of pressure is probably to cause gas to be dissolved into the pore water, mainly CO_2 gas. Thus, the effects of pressure are only limited to carbonate system. However, the amount of pressure acting on the gas and water probably is less than expected because extraction is performed to an open system (sampling vial).

The dissolution of CO_2 gas in the pore water by effect of pressure would form a weak acid solution that could cause pH or alkalinity changes and dissolve minerals. These processes would cause increases in calcium, magnesium, potassium and silica. However, no significant increases of these ions are seen as result of compression, being more evident an oxidation process. Thus, dissolution is not probable that occurs at these pressures. Besides, the changes in saturation indices of minerals phases indicating precipitation or dissolution by effect of pressure were analysed (see section 5.4). With respect to the expected mineral equilibria in Opalinus Clay according to their mineralogy, undersaturation only was observed for quartz. However, this effect was related by an effect of temperature and can be corrected experimentally or by geochemical modelling. Oversaturation of calcite can be explained in terms of degassing of the samples and corrected by geochemical modelling.

The second hypothesis of dilution by compression of clays and release of ion-deficient bound water (van Olphen, 1963), resulting in progressively decreasing ion concentration can not be seen in the range of pressures analysed in this work: 75 to 200 MPa. However, these data could be compared with other ones obtained in Pearson et al (2003), where pressures up to 510 MPa were applied in a core sample from borehole BWS-A6. In Figure 14, the variations in chloride concentration can be seen for different core samples up to squeezing pressures of 510 MPa. Lower chloride concentrations were obtained from pressures of 200 MPa, indicating that for pressures higher than 200 MPa double-layer water is squeezing out. This provokes the mixing of the true pore water (free pore water) and the outer layers of the double-layer water, diluting the ion concentration. The net result is a decrease of the concentration with increasing pressure. At higher pressures, the dimension of the flow channels seems to decrease resulting in a filtration of salts due to the membrane effect.

Therefore, it can be concluded that no ionic ultrafiltration, chemical fractionation, retardation of dissolved ions, salt-sieving or dilution of the pore water was not observed at the range of squeezing pressures analysed in this study. A threshold squeezing pressure of 175 MPa could be established for Opalinus Clay. It is recommended to use the minimum experimental time for obtaining the quantity of water required for chemical analysis in order to avoid oxidation processes. Isotopic fractionation due to increasing squeezing pressures were not analysed in this work. Only isotopic data from squeezed waters and in situ borehole waters could be compared.

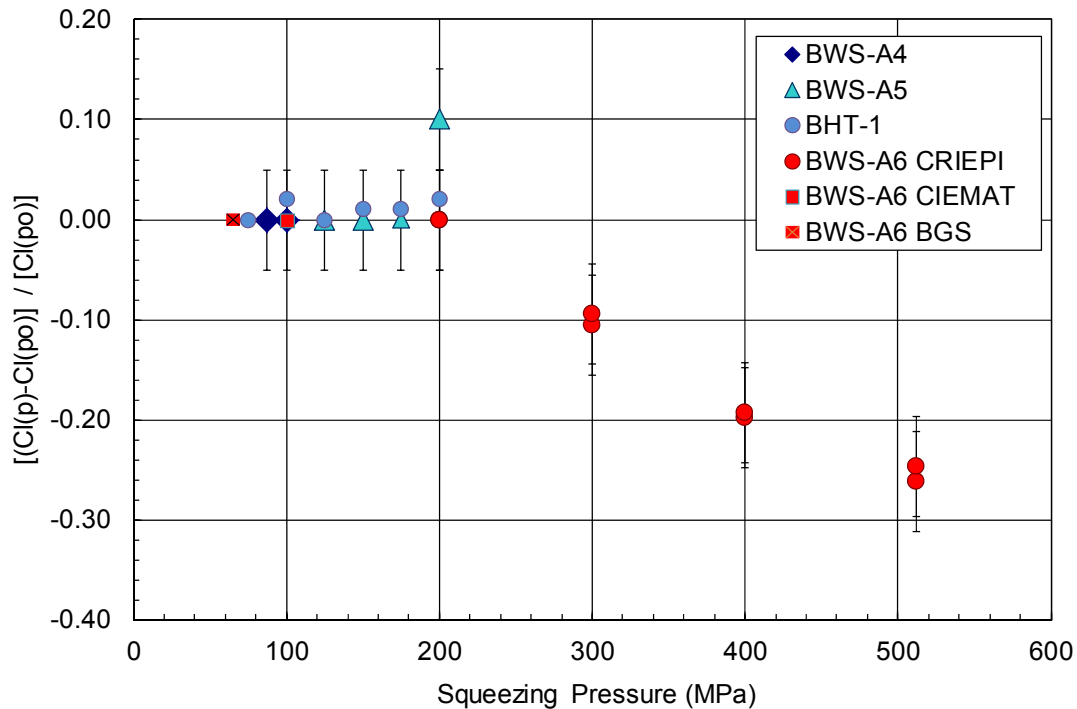


Figure 14. Deviation of chloride concentrations at high squeezing pressures (Cl(p)) from those measured at lowest pressure yielding water (Cl(po)) for squeezing carried out at CIEMAT (BWS-A4, BWS-A5, BWS-A6, BHT-1), CRIEPI and BGS (after Pearson et al., 2003)

5.6. Artifacts on pore water composition extracted by squeezing

5.6.1. Core sampling and preservation of the core samples

All of the *ex situ* pore water extraction techniques require collection and preservation of core material prior to testing and some form of sample preparation (Sachi et al., 2000; Mazurek et al., 2009). The drawback of the *ex-situ* and indirect methods to collect the clayrock pore water is the difficulty to achieve a rapid sampling to maintain the sediment/rock samples in the laboratory under *in situ* conditions. Improper sampling, storage and handling of the material, as well as inadequate precautions during these processes may induce errors by increasing the risk of changes in the geochemical character and composition of the pore water.

There are three main perturbation or artifact processes to take into consideration, although some of them are also involved in pore water extraction at *in situ* conditions in packed boreholes: a) contamination and modification of the rock material during borehole drilling (e.g. adsorption of the drilling fluid on the rock, oxidation arising from the drilling technique, or drying); b) modification of the pore water chemistry during storage (e.g. by oxidation, evaporative loss of moisture or bacterial growth); and c) contamination and modification of the sample during the extraction process (e.g. by

pressure, temperature or oxidation effects). The small pore water volumes involved together with the handling procedures may induce contamination and other changes in the sample characteristics that may affect the *in situ* or *real* chemical compositions that may be virtually impossible to estimate with any certainty.

In the context of Mont Terri Project, for overcoming artifacts of sampling, new experimental designs were proposed with time for both in laboratory and field *in situ* studies to minimize sample perturbations which affect the pH, the carbonate system and the redox equilibrium. The boreholes were never drilled with a fluid as dust evacuation for avoiding any modification of the chemical and isotopic composition of the pore water. As example of drillcore contamination, Edmud and Bath (1976) found the extent of fluid invasion in the cores limited to the outer 1-1.5 cm by using lithium-chloride tracer added to the drilling mud.

In the Mont Terri Rock Laboratory different types of air drilling fluids were used. Until 2002 the boreholes were drilled with air (boreholes BWS-A6, BWS-E4, BWS-E6, BWS-A4, BWS-A5, BDR-2). From 2002, the water sampling interval of the boreholes began to be drilled with nitrogen for avoiding possible alterations of the clayrock by oxidation (borehole BPC-1); and since 2009 with Argon gas to prevent modifications of the pore water and rock by oxidation and bacterial growth and disturbances (borehole BHT-1). As shown in Table 3, air or Ar drilling doesn't desaturated the rock, which can be seen in the degree of saturation of the rock. This value is 100% indicating a water filled saturated rock. Other processes, such as oxidation, couldn't be observed because prior to perform the laboratory tests, the core samples were prepared using a knife to scrape the outer annulus of the cores.

After borehole drilling, the main challenge for core preservation is related to avoid contact between the rock samples and the atmosphere (mainly oxygen and relative humidity from the air). Avoiding water losses is essential for preservation of full saturation in order to measure the gravimetric water content and indirectly the porosity; as well as for eluding desaturation of the rock and water evaporation which imply another chemical disturbance by precipitation of dissolved salts. Polyethylene bags were found highly contaminating by phthalate release (Griffault et al., 1996) and are less resistant to vacuum and more permeable to air. At Mont Terri, the core samples were preserved after drilling by *in situ* wrapping and protecting the drillcores in vacuum packered aluminium-coated foil bags (flushed with inert gases such as nitrogen or argon, then evacuated and sealed) to prevent water-loss or drying, oxidation, organic matter degradation as a result of UV radiation, CO₂ degassing and other gas exchange processes (modifying isotopic signals) during shipping and storage. The operation was performed as soon as possible to avoid evaporation.

At laboratory, the cores were stored and kept chilled at 4°C (not freezing) in a refrigerator after reception for a long-term conservation of the cores, avoiding microorganisms growth. However, this procedure may alter the *in situ* temperature chemical conditions especially in samples stored for too long prior to testing.

From the results obtained in this work, the conservation of the samples resulted ideal because although the core samples were stored several months until their analysis, even one sample during four years (Table 6), the degree of saturation was maintained at 100% over time (Table 3), indicating no appreciable dehydration or evaporation prior to start the analysis, which would result in the precipitation of dissolved salt on the core surface and in increased pore water concentrations. Besides, most of the squeezed pore waters show sulphate concentrations similar to *in situ* values (Figure 5) and Cl/SO₄²⁻ ratios close to seawater, which indicate no signs of oxidation neither during storage nor during squeezing (see later). Therefore, wrapping the rock in at vacuum aluminium foil bags was successful for preventing these types of artifacts.

5.6.2. Effects of changing pressure

Some decompressional changes may occur in the cores when they are taken out from the sedimentary/rock formation after borehole drilling due to the lack of confining lithostatic pressure. They may affect to mechanical properties, such as variations in dry density, or to the geochemical equilibria affecting the distribution of some chemical constituents in the pore water due precipitation processes, the degassing of the sample (exsolution of gases) if the gas partial pressures in the pore water are higher than in the surrounding environment, or the entrance of atmospheric gases, such as oxygen.

Decompressional effect is quite dependent of the type of sediment. Changes in dry density may much higher and appreciable in soft materials, such as marine and Recent clayey sediments, than in indurated mudrocks with very low porosity, as occurs in Opalinus Clay. In carbonate-rich sediments, the change in pressure may provoke non reversible changes in the carbonate equilibria, because of its well-known pressure dependent equilibrium constant, leading to precipitation of CaCO_3 and, as consequence, deviations from the *in situ* Ca and alkalinity concentrations in the pore water. This effect does not occur in carbonate-poor sediments as it was observed in marine sediments, where large changes in pressure occur when the core is raised to the surface from the sea floor. i.e., abyssal depths (Murray et al., 1980; Jahnke et al., 1982; de Lange, 1986).

CO_2 -degassing also affects to the carbonate system, leading to the loss of TIC, Ca and increased pH, as well as the precipitation of carbonates.

In this work, evaluation of geochemical changes due to decompressional changes were evaluated by the saturation index of carbonates, and taking into account the mineralogy of the clayrock which regulate the chemical equilibrium of the pore waters.

Regarding the effect of the squeezing pressure, a threshold pressure should be determined for each type of clayrock for avoiding ultrafiltration process. In this work a threshold squeezing pressure of 175 MPa was established.

5.6.3. Effects of changing temperature

If the temperature of the sediments during core drilling or pore water extraction (by squeezing or leaching, etc.) deviates too much from the *in situ* temperature condition, the solid-liquid equilibrium conditions may change; causing a large difference between the extracted and the *in situ* concentrations for some ions. The temperature effect is dependent on the type of sediment involved, i.e., depends on the amount and type of clay minerals (Sayles and Manheim, 1975; Sayles et al., 1973; de Lange et al., 1992), as well as on the difference of temperatures between *in situ* conditions and core drilling or water extraction (Bischoff et al., 1970; Gieskes, 1975; Masuzawa et al., 1980).

Most of the studies about the influence of temperature on the pore water due to core sampling or the extracting method were performed for marine sediments where the differences between squeezing temperatures and *in situ* temperatures are about 20 °C. In the case of Recent sediments (estuarine, lacustrine, etc.), consolidated and unconsolidated clayrocks, the changes in temperature are not so high. For example, the temperature in the Opalinus Clay rock formation is about 13°C, whereas in the Callovo-Oxfordian is 25°C and in the Vembanad estuarine sediments (India) the temperature ranges from 29° C to 31° C. These temperatures are closer to room temperature.

Warming of marine sediments by raising the temperature about 20°C during core sampling and squeezing, gave enrichments of potassium (13.3%), silica (51%) and boron (29%); and depletions of calcium (4.9%) and magnesium (2.5%), suggesting a change in the bicarbonate content to balance the electroneutrality of the solution, although no consistent changes in alkalinity and phosphate were found, as well as in anion concentrations (Manhelschof et al., 1969; Bischoff et al., 1970; Fanning and Pilson; 1971; Sayles et al., 1973; Gieskes, 1973). Absolute changes in warming followed the magnitudes: $\text{Mg} \geq \text{Na} > \text{K} > \text{Ca} > \text{Si} > \text{Sr} > \text{B}$, with monovalent cations showing enrichments and divalent cations showing depletion.

The temperature dependency of the cations and anions seems to be due to the temperature dependency of cation-exchange and anion-exchange equilibrium between clay minerals and pore water, i.e., to changes in ion-exchange selectivity as a function of temperature. However, most of these changes seem to be completely reversible on re-equilibration and storage of the core samples at *in situ* temperatures or performing the squeezing tests by using thermoregulation (Kalil and Goldhaber, 1973; Masuzakada et al., 1980).

In this work, the Opalinus Clay core samples were stored in a refrigerator at 4°C after their reception at laboratory. Because of the squeezer is not thermoregulated and the pore water samples were extracted at laboratory temperature (22-25°C), the temperature effects were evaluated by comparing the squeezed data with those obtained by BGS, which used a thermoregulated squeezing cell; as well as checking the saturation index of minerals such as quartz (see above). Potassium enrichments in the extracted pore waters were systematically detected; as well as an undersaturation in quartz. However, the effect of temperature is reversible if *in situ* temperatures are taken into account during water extraction or in geochemical modelling. Temperature changes inside the cell and of the extracted water as result of squeezing pressure during compaction seem to be negligible if the laboratory temperature is stabilized (20-22°C).

5.6.4. *Effects of CO₂ degassing: how to solve the pH problem?*

Degassing and/or CO₂ degassing may occur whenever the gas partial pressures in the pore water are higher than the surrounding ones. This is the case of the Opalinus Clay pore water which has a partial pressure of CO₂ around 10^{-2.2} atm. (Pearson et al., 2003), higher than the CO₂ atmospheric partial pressure (10^{-3.5} atm.).

Degassing is a very rapid phenomenon which has no effect on alkalinity but increase pH and decrease the TIC content. CO₂ loss may lead to the loss of total dissolved carbonates, precipitation of carbonates in the pore spaces, subtractions of calcium from the solution and at the end modification in the cation concentration in the pore water from cation exchange reactions in clay minerals. Carbonate precipitation affect to alkalinity and TIC.

CO₂ degassing may occur in the core samples during sampling due to a decompaction of the rock (loss of lithostatic pressure) and during transport if especial efforts are not made to minimize gas losses by wrapping the core material inside Al-coated sealed bags. However, degassing affect also water sampling, both from boreholes (Pearson et al., 2003) and squeezing. As long as water is in contact with the clay, pH of the pore water will be buffered by water/rock interaction, but as soon as it is separated from the rock, the pH will start rising. As a consequence, pH measurements are usually not reliable.

Changes in pH (increased values) due to CO₂ degassing was a problem detected in this work. For example, the water sample obtained at 75 MPa in the BHT-1 core sample, which apparently was not affected by an oxidation process had a higher pH value than that expected in the *in situ* pore waters of the Opalinus Clay. This may be correlated with a degassing process of the water sample during their collection inside the septum vials (see below).

5.6.5. *Effects of changing redox conditions: Oxidation, contamination*

There is a risk of changes in the geochemical character of clayrocks induced by exposure to the atmosphere. The drawback of indirect or ex-situ methods is the need for maintaining the sediment under anoxic conditions to obtain a pore water representative of the sedimentary environment. Some components of clayrocks are very sensitive to oxygen, especially pyrites and organic matter (Pearson et al., 2003). Besides, the oxidation of the core samples induces immediate changes in the redox-sensitive chemical species of various dissolved elements in the pore water, such as dissolved sulfides, sulfur, phosphate (Bray et al., 1973), manganese and iron (Troup et al, 1974), with their subsequent

precipitation of by-products mineral phases which influence in other species parameters (pH, CO₂, alkalinity). Special precaution must be taken during drilling, storage and prior to performing any laboratory test.

Because the outer parts of the cores are frequently contaminated due to drilling fluids and smearing of sediments along the core tube, is recommended to select the interior portions of the cores, which show the least sign of disturbance and deformation, for sampling pore water. Additionally, it is essential to minimize the core sample storage time prior to any tests including squeezing (Bishchoff et al., 1971). In order to minimize possible confounding factors resulting from chemical changes after sampling, sediment storage should be as short as possible (i.e., less than two weeks) and preferably less than 24 hours.

In this work, special cares were taken during the handling of the rock samples in the laboratory and during the preparation of the core samples prior to tests or during the performance of experimental studies. However, these cares were improved over time. For example, for all geochemical, mineralogical and squeezing analyses, the outer annulus of core material was trimmed with a knife and discarded to try to maintain uncontaminated rock prior to extraction tests. The core samples analysed between 1997 and 1999, these operations were performed at ambient laboratory conditions minimizing the contact with the atmosphere (less than 1 hour), and using of non potentially contaminated tools or devices, However, for core samples BDR-2 and BHT-1 all the operations for preparation and treatment prior to analysis (trimming, crushing, grinding, etc.), as well as the performance of experimental studies for these core samples, such as leaching tests and exchange cation population, were carried out inside an anoxic glove box (< 1 ppm atmospheric O₂).

Squeezing tests were performed at ambient conditions. However, a small stress of 1 to 10 MPa was initially applied to remove most of the atmospheric gas from the cell and allow the sample to bed in most of the squeezing tests, and then the system was closed with a syringe. In the case of the core samples from boreholes BDR-2 and BHT-1, instead of a syringe, a vacuum septum vial was used; and the sampling vial and squeezer cell were flushed with Ar gas prior to start the tests for avoiding oxidation problems. Furthermore, short duration tests used for performing a squeezing tests avoid oxidation process, as it was observed in this work.

There is no an indication of contamination of the pore water by corrosion of the metal of the cell and the sintered filters. Values of chromium and nickel are usually below detection limits in the pore water samples.

6. Anion accessible porosity

By knowing the anion-accessible porosity or geochemical porosity, the anion concentration in pore water can be inferred from its concentration in the aqueous leaching solution at a specific S:L ratio, by assuming that all Cl⁻, Br⁻ and SO₄²⁻ leached in the aqueous extracts originates from pore water. In Opalinus Clay this is reliable for Cl⁻ and Br⁻, but not for SO₄²⁻ and bicarbonate content. Dissolution of carbonates and soluble sulfates (coming from pyrite oxidation) affects the concentration of these ions in aqueous extract tests (see section 5.2.2).

An important issue in order to model the pore water chemistry in a clayey media is to determine the respective volume accessible to cations and anions, i.e, the amount of water actually available for chemical reactions/solute transport. This amount is usually referred as anion accessible porosity (Pusch et al., 1999), geochemical porosity (Pearson, 1998) or external porosity (Muurinen, 1994; Fernández et al., 2004). The anion accessible porosity is the ratio between the pore water volume containing Cl-bearing pore water and the total volume of a sample (Pearson, 1998; Pearson et al., 2003b). The Cl porosity is lower than the total physical porosity, because clays have different types of water (interlayer water, adsorbed water and free water), and ions can be affected by anionic exclusion processes. The anion-accessible porosity only includes the free water and maybe some of the diffuse layer and surface-sorbed water; while the total physical porosity includes both the external and internal water.

In order to calculate the anion accessible porosity or Cl accessible porosity (ϵ_{Cl}), the following relationship was used which relates leaching data (Cl content of the rock, Cl_{rock}), and the chloride content of the pore water extracted by squeezing (Cl_{pw}):

$$Cl_{pw} \left(\frac{\text{mol Cl}}{\text{L pore water}} \right) = \frac{Cl_{rock} \left(\frac{\text{mol Cl}}{\text{kg bulk}} \right) \cdot \rho_{\text{bulk, dry}} \left(\frac{\text{kg bulk}}{\text{L bulk rock}} \right)}{\epsilon_{Cl} \left(\frac{\text{L Cl bearing pore water}}{\text{L bulk rock}} \right)} \quad \text{Eq. 14}$$

By using the chloride content of the pore water extracted by squeezing (Table 8, Table 9) and the chloride inventories (Table 10), the different porosities were calculated for each sample (Table 13). The anion accessible porosity ranged from 6.5 to 11.7 %vol., being the average value in the Shaly facies of the Opalinus Clay of 9.7 %vol, and the mean Cl porosity/Water loss porosity ratio of 0.57. This is in agreement with the values found in the Opalinus Clay formation. In most of the core samples from Mont Terri, this ratio ranges from 0.5 to 0.7, although a value of 0.55 is frequently used (Pearson et al., 2003). Through diffusion experiments Van Loon et al. (2003) found values of chloride accessible porosity in Opalinus Clay of around 7.2, which are in agreement with the data obtained in this work.

Table 13. Anion accessible porosity (Cl porosity/water loss porosity)

Core sample	Cl (leaching) mol/kg rock	Pore water Cl (squeezed sample) mol / L H ₂ O	Total Porosity (% vol.)	Cl porosity (% vol)	Cl porosity/ Water loss porosity
BWS-E6 m. 3.05-3.40	1.55·10 ⁻²	3.10·10 ⁻¹	17.3	11.2	0.64
BWS-A6 m. 4.10-4.30	1.24·10 ⁻²	3.38·10 ⁻¹	16.0	8.4	0.53
BWS-A4 m. 6.99-9.94	1.45·10 ⁻²	2.82·10 ⁻¹	17.0	11.7	0.69
BWS-A5 m. 7.40-7.79	1.16·10 ⁻²	2.82·10 ⁻¹	16.2	9.4	0.58
BHT-1 m. 12.4-12.9	1.18·10 ⁻²	2.76·10 ⁻¹	16.9	9.7	0.57
BDR-2 m. 5.93-6.36	6.88·10 ⁻³	1.72·10 ⁻¹	15.6	9.2	0.59
BWS-E4 m. 4.28-4.65	1.97·10 ⁻³	7.04·10 ⁻²	14.4	6.5	0.45

7. CONCLUSIONS

Collection of representative pore water solutions in clayrocks is one of the main objects of any hydrogeochemical research program in argillaceous formations. However, recovering the pore water solution representative of *in situ* conditions from low permeable and low water content systems is very difficult and sometimes impossible. Measuring the *in situ* composition of clayrocks pore water from packered boreholes is expensive, compared to laboratory tests. Moreover, ex-situ water collection methods are often necessary when *in situ* water collection is not viable, or when a brief sampling time is critical for chemical characterization. Therefore, squeezing technique can then be a good alternative method to obtain the pore water composition.

Pore water extraction by squeezing from clay sediments, clayrocks and soils dates back more than 115 years, and although different studies have shown that, so long as core sample collection, handling and preservation methods are satisfactory, pore waters obtained by squeezing tend to be representative of *in situ* conditions; this technique is criticized, and usually is thought that the solution obtained under great pressures would be of doubtful value. Apart from problems which are common in other extraction methods, even in *in situ* tests (oxidation, degassing, changes in temperature, etc.); squeezing technique could add intrinsic problems, such as squeezing pore waters would be diluted due their mixture with double-layer water or the possible existence of a membrane or filtering effect through charge-net clay membranes in highly consolidated sediments.

In this work, a study of the squeezing technique was performed on Opalinus Clay samples from Mont Terri (Switzerland), which is a low-porosity, low water content (< 8%) and highly consolidated clayrock. To validate the squeezing technique for the analysis of the ion and isotope data different methods were used. The first procedure was to check the reproducibility of the data with the same technique at different laboratories. The second was to compare quantitatively the results obtained with other method, such as *in situ* tests. The third was to analyse the factors and possible artefacts which could influence on the reliability of the pore water chemical composition extracted by squeezing, such as pressure, degassing, oxidation, etc.

The squeezing technique is a valuable method for obtaining the pore water chemistry from indurated clayrocks if a threshold squeezing pressure is taken into account for avoiding the extraction of the diluted double-layer water. Under favourable conditions, squeezing may yield sufficient water to perform a complete chemical and isotopic analysis of the pore water. A global view of the data indicates that the squeezing technique is quite reproducible even though different squeezing pressures were used at different laboratories (at 70 MPa at BGS and between 75 and 150 MPa at CIEMAT). For the conservative elements such as chloride and bromide, the concentrations are similar. In Opalinus Clay, no significant changes in the chemical composition of the Opalinus Clay pore waters were obtained as the pressure was raised up to 200 MPa. In this clayrock with no swelleable clay minerals, no ionic ultrafiltration, chemical fractionation or anion exclusion was found in the range of pressures analysed: 70-200 MPa. Pore waters extracted in this range of pressures do not decrease in concentration, which would indicate a dilution of water by mixing of the free pore water and the outer layers of double layer water (Donnan water). A threshold (safety) squeezing pressure of 175 MPa was established for avoiding membrane effects (ion filtering, anion exclusion, etc.) from clay particles induced by increasing pressures.

The chemical and isotopical data from squeezed water in the range of pressures between 70 and 75 MPa can be considered representative for this formation because they are comparable with *in situ* borehole collected water. This is true if some artifacts are avoided during the storage of the core samples and during the extraction process.

Problems related to oxidation processes of pyrite have been detected when the time used up in squeezing tests is long (100 and 162 days), which affected the sulfate concentration in the pore water, as well as alkalinity, and cations concentrations. In squeezing tests performed over shorter periods (≈ 15 days), this alteration does not occur.

Potassium enrichments in the squeezed pore waters and quartz undersaturation seem to be related to changes in the temperature of the core samples from *in situ* environments. However, these changes are

reversible if *in situ* temperatures are taken into account during storage or water extraction. Other artefacts, such as CO₂ degassing and quartz undersaturation can be corrected by geochemical modelling.

Squeezing data of conservative ions are instrumental for the determination of the anion-accessible porosity fraction of physical porosity necessary for geochemical modelling purposes. In Opalinus clay anion-accessible porosity values ranged between 53% and 69%.

Besides, squeezing method also provides information on the interactions between the pore water solutes and the rock, mineral reactions and ion exchange, which are key factors influencing solute transport. It seems that both chemical and isotopic data from squeezed pore waters in Opalinus Clay reproduce the mechanisms governing the concentration changes in pore water components, as well as gives information about the diagenetic processes occurred in the clayrock over time. This allows the validation of modelling of water and solute flow through low permeability environments.

8. ACKNOWLEDGMENTS

This work has been carried out at the Mont Terri Underground Research Laboratory (Switzerland). CT and EG acknowledge funding from ANDRA under the BRGM/ANDRA scientific partnership agreement. We acknowledge the Chemical Department at CIEMAT, as well as the Swiss Federal Office of Water and Geology, the Mont Terri Consortium, the Swiss authorities, and especially to Paul Bossart, the director of the Mont Terri Project; for having enabled us to perform this work in their experimental site. A special thanks to people from Swisstopo for their great help and especially to Christophe Nussbaum, the Mont Terri Project Manager.

9. REFERENCES

- Adams, D.D., 1994. Sediment pore water sampling. IN: Handbook of Techniques for sediment sampling. Mudrock, A., and MacKnight (eds). 2nd Edition. CRC Press Inc. Chapter 7, pp. 171-202.
- Adams, L.H., Williamson, E.D. and Johnston, J., 1919. The determination of the compressibility of solids at high pressures. J. Am. Chem. Soc., 41: 12-42.
- Alonso, C., Antón-Pacheco, C., Baretino, D., Cabrera, F., Fernández, A. M., Fernández, J. E., García-Gutiérrez, M., Giráldez, J. V., Girón, I. F., López-Pamo, E., Moreno, F., Ordóñez, R., Pelayo, M., Rivas, P., Vanderlinden, K. y Villar, M. V., 2001: Los suelos del Guadiamar: estudios de caracterización y de la evolución de los suelos contaminados por el lodo. The Guadiamar soils: characterization and evolution of soils affected by the pyritic sludge. Boletín Geológico y Minero. Volumen especial 112 (Las aguas y los suelos tras el accidente de Aznalcóllar.), 163-198.
- Altmann, S., 2008. Geochemical research: A key building block for nuclear waste disposal safety cases. Journal of Contaminant Hydrology, 102, pp. 174-179.
- Amman, L., Bergaya, F., Lagaly, G. 2005. Determination of the cation exchange capacity of clays with copper complexes revisited. Clay Minerals 40, 441-453.
- Andra, 2005. Dossier 2005 Argille. Synthesis. Evaluation of the feasibility of a geological repository in an argillaceous formation. Meuse/Haute-Marne site. ANDRA Report Series.
- Appelo, C.A., Vinsot, A., Mettler, S., Wechner, S., 2008. Obtaining the porewater composition of a clay rock by modelling the in- and out-diffusion of anions and cations from an in-situ experiment. Journal of Contaminant Hydrology, 101, pp. 67-76.

- Arcos, D., Bruno, J., Peña, J., Turrero, M.J., Fernández, A.M^a, 2001. 1-D reactive transport model for the Opalinus Clay. Proceedings of the tenth international symposium on water-rock interaction. WRI-10. Villasimius, Italy, 10-15 July 2001. Edited by R. Cidu. A.A. Balkema Publishers, pp. 1303-1306.
- Bath, A. H., Ross, C.A.M., Entewisle, D. C., Cave, M. R., Green, K.A., Reeder, S., Fry, M.B., 1989. Hydrochemistry of porewaters from Lower Lias siltstones and limestones at the Fulbeck site. Fluid Processes Research Group. British Geological Survey. Technical Report WE/89/27. NSS/R171, 55 pp.
- Bath, A.H., Pearson, F.J., Gautschi, A., Waber, H.N., 2001. Water-rock interactions in mudrocks and similar low permeability material. In: Proc. 10th Int. Symp. on Water-Rock Interactions, Villasimius, Sardinia. A.A. Balkema, Rotterdam, pp. 3-12.
- Beucaire, C., Pitsch, H., Toulhoat, P., Motellier, S. and Louvat, D., 2000. Regional fluid characterisation and modelling of water-rock equilibria in the Boom clay Formation and in the Rupelian aquifer at Mol, Belgium. Applied Geochemistry, 15, 667-686.
- Bender, M., Martin, W., Hess, J., Sayles, F., Ball, L, Lambert, C., 1987. A whole-core squeezer for interfacial pore water sampling. Limnol. Oceanogr., 32(6), 1214-1225.
- Bischoff, J.L., Greer, R.E., Luistro, A.O., 1970. Composition of interstitial waters of marine sediments: temperature of squeezing effect. Science 167, 1245-1246.
- Blanc, P.; Lassin, A.; Piantone, P.; Azaroual, M.; Jacquemet, N.; Fabbri, A., Gaucher, E. C., 2012.
- Bossart, P, Thury, M., 2008. Mont Terri Rock Laboratory – Project, Programme 1996 to 2007 and Results. Reports of the Swiss Geological Survey No. 3 – Swiss Geological Survey, Wabern, 2008, 193 pp.
- Böttcher, G., Brumsack, H.J., Heinrichs, H., Pohlmann, M., 1997. A new high-pressure squeezing technique for pore fluid extraction from terrestrial soils Water, Air, Soil Pollution , Volume 94 (3), 289-296.
- Bradbury, M.H., Baeyens, B., 1998. A physico-chemical characterisation and geochemical modelling approach for determining porewater chemistries in argillaceous rocks. Geochim. Cosmochim. Acta 62, pp. 783-795.
- Bray, J.T., Bricker, O.P., Troup, B.N., 1973. Phosphate in interstitial waters of anoxic sediments: oxidation effects during sampling procedure. Science 180, 1362-1364.
- Bridgman, P.W., 1918. Stress-strain relations in crystalline cylinders. Am. J. Sci., 45: 269-280.
- Bridgman, P.W., 1937. The resistance of nineteen metals to 30,000 kg/cm². Proc. Am. Acad. Arts Sci., 72, 157.
- Brightman, M.A., Bath, A.H., Cave, M.R., Darling, W.G., 1985. Pore fluids from the argillaceous rocks of the Harwell Region. Fluid Processes Research Group. British Geological Survey. Report FLPU 85-6, 77 pp.
- Bruevich, S.V. (Ed.), 1966. Chemistry of interstitial waters in sediments of the Pacific Ocean (Russ.), In Khimiya Tikhogo Okeana Moscow: Izdat. Akad. Nauk, 253-358.
- Bundy, F.P., 1962. General principles of high-pressure apparatus design. In: R.H. Wentrof Jr. (Editor), Modern Very High Pressure Techniques. Butterworths, London, England, pp.1-24.
- Buneeva, A.N., Kryukov, P.A. and Rengarten, E.V., 1947. Experiment in squeezing out of solutions from sedimentary rocks. Dokl. Akad. Nauk S.S.S.R., 57(7), 707-709.
- Burgess, P.S., 1922. The soil solution extracted by Lipman's direct-pressure method, compared with 1:5 water extracts. Soil Sci. 14, pp. 191-216.
- Casagrande, A., 1932. The structure of Clay and its importance in foundation Engineering. Journal of the Boston Society of Civil Engineers, v. 19, p. 168.

- Chilingar, G.V. and Knight, L., 1960. Relationship between pressure and moisture content of kaolinite, illite and montmorillonite clays. *Bull. Am. Assoc. Pet. Geologists* 44, 101-106.
- Chilingar, G.V., Rieke III, H.H. and Robertson Jr., J.O., 1963a. Relationship between high overburden pressures and moisture content of halloysite and dickite clays. *Geol. Soc. Am. Bull.*, 14(8), 1041- 1048.
- Chilingar, G.V., Rieke III, H.H. and Robertson Jr., J.O., 1963b. Degree of hydration of clays. *Sedimentology*, 2(4): 341-342.
- Chilingarian, G. V., Rieke, H. H., 1968. Data on consolidation of fine grained sediments: *J. Sedim. Petrol* 38, 811-816.
- Chilingarian, G. V., Sawabini, C. T., Rieke, H. H., 1973. Effect of compaction on chemistry of solutions expelled from montmorillonite clay saturated in sea water: *Sedimentol.* 20, 391-398.
- CRC Handbook of chemistry and physics, 1994. Lide David R. (Ed.). CRC Press, Inc.
- De Craen, M., Van Geet, M., Wang, L., Put, M., 2004a. High sulphate concentrations in squeezed Boom Clay pore water: evidence of oxidation of clay cores. *Physics and Chemistry of the Earth*, 29, pp. 91-103.
- De Craen, M., Wang, L., Van Geet, M., Moors, H., 2004b. Geochemistry of Boom Clay porewater at the Mol site. Scientific Report, SCK-CEN-BLG-990, 180 pp.
- de Lange, G.J. Cranston, R.E., Hydes, D.H. and Boust, D. 1992. Extraction of pore water from marine sediments: A review of possible artifacts with pertinent examples from North Atlantic. *Mar. Geol.*, 109, 53-76.
- de Lange, G.J., 1986. Chemical composition of interstitial water in cores from the Nares abyssal plain (Western North Atlantic). *Oceanologica Acta* 9, 159-168.
- de Lange, G.J., 1992. Shipboard routine and pressure-filtration system for pore water extraction from suboxic sediments. In: J.J. Middelburg and S. Nakashima (Editors), *The Geochemistry of North Atlantic Abyssal plains*. *Mar. Geol.*, 109, pp 77-81.
- de Windt, L., Cabrera J., Boisson, J.Y., 1998. Hydrochemistry in an indurated argillaceous formation (Tournemire tunnel site, France). *Water-Rock Interaction*, Arehart & Hulston (eds). Balkema.
- Devine, S.B., Ferrel, R.E., Jr., and Billings, G.K., 1973, The significance of ion exchange to interstitial solutions in clayey sediments: *Chemical Geology*, v. 12, p. 219-228.
- Di Bonito, M., 2005. Trace Elements in Soil Pore Water: A Comparison of Sampling Methods, Ph.D. thesis, University of Nottingham, Nottingham (<http://etheses.nottingham.ac.uk/archive/00000123/>).
- Di Bonito, M., Breward, N., Crout, N, Smith, B, Young, S., 2008. Overview of Selected Soil Pore Water Extraction Methods for the Determination of Potentially Toxic Elements in Contaminated Soils: Operational and Technical Aspects. In: *Environmental Geochemistry. Site Characterization, Data Analysis and Case Histories*. De Vivo, B, Belkin, H.E., Lima, A. (Eds), pp. 213-249.
- Edmunds, W.M., Bath, A.H., 1976. Centrifuge extraction and chemical analysis of interstitial waters. *Environ. Sci. Technol.*, 10, 467-472.
- ENRESA, 2000. FEBEX Project. Full-scale engineered barriers experiment for a deep geological repository for high level radioactive waste in crystalline host rock. Final Report. Technical Publication ENRESA 1/2000, 354 pp. Madrid.
- ENRESA, 2006. Full-scale Engineered Barriers Experiment. Updated Final Report 1994-2004. Technical Publication ENRESA 05-0/2006, 590 pp. Madrid.

- Entwisle, D.C., Reeder S., 1993. New apparatus for pore fluid extraction from mudrocks for geochemical analysis. In: *Geochemistry of Clay-Pore Fluid Interactions*. Chapter fifteen, pp. 365-388. Manning D.A.C., Hall P. L. and Hughes C.R. (eds). Chapman&Hall.
- Entwisle, D.C., Reeder, S., Bath, A.H., Ross, C.A., 1989. Techniques for the characterization of solutes in drillcore from mudrocks. Natural Environment Research Council. Fluid Processes Research Group. British Geological Survey. Report Number WE/89/29C.
- Fanning, K.A. and Pilson, M.E.Q., 1971, Interstitial silica and pH in marine sediment: Some effect of sampling procedure. *Science*, 173, pp 1228-1231.
- Fatt, I., 1953. The effect of overburden pressure on relative permeability. *Trans. Am. Inst. Min. Metall. Engrs.*, 198, 3 25-326.
- Fernández A.M^a, 2004. Caracterización y modelización del agua intersticial en materiales arcillosos: Estudio de la bentonita de Cortijo de Archidona. Ph. D. Thesis. CIEMAT, Madrid, 505 pp.
- Fernández, A.M., Melón, A., Sánchez-Ledesma, Gaucher, E., Tournassat, C., Altmann, S., Vinsot, A., Maes, N., de Craen, M., Leupin, O., Wersin, P., Astudillo, J., 2009. Study of different Argillaceous Formations performed in the context of the FUNMIG Project: Pore Water Chemistry and Physical, Mineralogical and Geochemical Properties in Boom Clay, Callovo-Oxfordian, Opalinus Clay and Boda Claystone rock samples. *Publicación Técnica de Enresa 05/2009*, 214 pp.
- Fernández, A.M., Villar, M.V., 2010. Geochemical behaviour of a bentonite barrier in the laboratory after up to 8 years of heating and hydration, *Applied Geochemistry*, Volume 25(6), 809-824.
- Fernández, A.M^a, Baeyens, B., Bradbury, M., Rivas, P., 2004. Analysis of the pore water chemical composition of a Spanish compacted bentonite used in an engineered barrier. *Physics and Chemistry of the Earth*, Vol. 29, 105-118.
- Fernández, A.M^a, Bath, A., Waber, H.N., Oyama, T., 2003. Annex 2: Water Sampling by Squeezing Drillcores. In: Pearson et al., 2003. *Geochemistry of Water in the Opalinus Clay Formation at the Mont Terri Rock Laboratory*. FOWG N° 5, pp. 171-199.
- Fernández, A.M^a, Rivas, P.; Cuevas J., 2001. Pore water chemistry of the FEBEX bentonite. *Mat. Res. Soc. Symp. Pro.* 663, pp. 573-588.
- Fernández, A.M^a, Rivas, P.; Cuevas J., 2001. Pore water chemistry of the FEBEX bentonite. *Mat. Res. Soc. Symp. Pro.* 663, pp. 573-588.
- Fontanive, A., Gragnani, R., Mignuzzi, C., Spat, G., 1993. Chemical composition of porewaters in Italian Plio-Pleistocene clayey formations. In: *Geochemistry of Clay-Pore fluid interactions* (Manning D.A.C., Hall P.L. and Hugues C.R. Eds.), *The Mineralogical Society Senes* 84, pp. 389-411.
- Gann, D.P., 1965. Changes in Ionic Concentration of Effluent from Compaction of Clay. Thesis, Univ. Houston, Houston, Texas, 96 pp.
- Gaucher E., Tournassat C., Pearson F.J., Blanc P., Crouzet C., Lerouge C. et Altmann S., 2009. A robust model for pore-water chemistry of clayrock. *Geochimica et Cosmochimica Acta* 73, 6470–6487.
- Gaucher, E.C., Fernández, A.M., Waber, H.N., 2003. Rock and Mineral Characterization of the Opalinus Clay Formation. In: Pearson et al., 2003. *Geochemistry of water in the Opalinus Clay Formation at the Mont Terri Rock Laboratory*. Swiss Federal Office for Water and Geology Series, N° 5, pp. 281-303.
- Giardini, A.A., Tydings, J.E. and Levin, S.B., 1960. A very high-pressure high-temperature research apparatus and the synthesis of diamond. *Am. Mineralogist*, 45(1-2): 217-221.

- Gieskes, J.M., 1975. Chemistry of interstitial waters of marine sediments. *Annual Review of Earth and Planetary Sciences* 3, 433-453.
- Gola, G., 1910. Saggio d'una terra osmótica dell'edafismo. *Annali di Botanica*, 8, 275-548
- Griffault, L., Merceron, T., Mossman, J.R., Neerdael, B., De Canniere, P., Beaucaire, C., Daumas, S., Bianchi, A., Christen, R., 1996. Acquisition et regulation de la chimie des eaux en milieu argileux pour le projet de stockage de dechets radioactifs en formation geologique. *Projet Archimede-Argile*. CEC, EUR 17454, 176 pp.
- Hall, H.N., 1953. Compressibility of reservoir rocks. *Trans. Am. Inst. Min. Metall. Engrs.*, 198, 309-311.
- Hall, H.T., 1958. Some high-pressure, high-temperature apparatus design considerations: Equipment for use at 100,000 atm and 3000°C. *Rev. Sci. Instr.*, 29(4), 267-275.
- Hanshaw, B.B., Coplen, T.B., 1973. Ultrafiltration by a compacted clay membrane. II. Sodium ion exclusion at various ionic strengths. *Geochimica et Cosmochimica Acta* 22, 143-154.
- Hartmann, M., 1965. An apparatus for the recovery of interstitial waters from recent sediments. *Deep-sea Res.*, 12, 225-226.
- Heuer Jr., G.J., Knutson, C.F., Cavanaugh, R.J. and Bright, C.W., 1965. Method and apparatus for measuring compressibility of porous material. *US. Patent* 3, 199, 341
- Higgins, J.D., Burger, P.A. and Yang, .C., 1996. The one-dimensional compression method for extraction of pore water from unsaturated tuff. *U.S. Geological Survey Water Resource Investigations Report* 96-4281, 34 pp.
- Hiscock, K.M., Tabatabai Najafi, M., 2011. Aquitard characteristics of clay-rich till deposits in East anglia, Eastern England. *Journal of Hydrology* 405, 288-306.
- Horseman, S.T., Volckaert, G., 1996. Disposal of radioactive wastes in argillaceous formations. In: *Engineering Geology of Waste Disposal*. Bentley, S.P. (ed.). Geological Society Engineering Geology, Special Publication No. 11, pp. 179-191.
- Iyer, B., 1990. Porewater extraction: comparison of saturation extract and high pressure squeezing. In: *Physico-chemical aspects of soil and related materials*, ASTM Spec. mibl. 1095, pp. 159-170.
- Jackson, M.L., 2005. *Soil Chemical Analysis. Advanced course. Revised Second Edition*. Parallel Press. University of Wisconsin-Madison Libraries. Madison, Wisconsin, 930 pp.
- Jahnke, R.A., 1988. A simple, reliable and inexpensive pore water sampler. *Limn. and Ocean.*, 33, 483-487.
- Jahnke, R.A., Heggie, D., Emerson, S., Grundmanis, V., 1982. Pore waters of the central Pacific Ocean: Nutrient results. *Earth Planet. Sci. Lett.* 61, 233-256.
- Kalil, E.K., Goldhaber, M., 1973. A sediment squeezer for removal of pore waters without air contact. *J. Sediment. Petrol.* 43, 553-557.
- Kazintsev, E.A., 1968. Pore solutions of Maykop Formation of Eastern Pre-Caucasus and methods of squeezing of pore waters at high temperatures. In: G.V. Bogomolov et al. (Editors), *Pore Solutions and Methods of Their Study (A symposium)*. Izd. Nauka i Tekhnika, Minsk, pp.178-190.
- Kennedy, G.C., 1950. Pressure-volume-temperature relations in water at elevated temperatures and pressures. *Am. J. Sci.*, 248(8): 540-564.
- Kiho, K., Oyama, T., Mahara, Y., 1999. Production of the compaction type pore water extraction apparatus and its implication to the deep-seated sedimentary rock. *J. Japan Soc. Eng. Geol.* 40, pp. 260-269.
- Krahn, J., Fredlund, D. G., 1972. On total, matric and osmotic suction. *Soil Science*, 114(5), 339-

348.

- Kriukov, P.A., 1947. Recent methods for physicochemical analysis of soils; methods for separating soil solutions (Russ.). In: Rukovodstvo dlya polevykh i laboratornykh issledovaniy pochv. Moscow Izdat. Akad. Nauk, SSSR, 3-15.
- Kriukov, P.A., Manheim, F.T., 1982. Extraction and investigative techniques for study of interstitial waters of unconsolidated sediments: a review, in *The Dynamic Environment of the Ocean Floor*. Fanning, K.A. and Manheim F.T. (Eds), pp. 3-26.
- Kriukov, P.A., Zhuchkova, A.A., Rengarten, E.V., 1962. Change in the composition of solution preserved from clays and ion exchange. *Earth Science* 144, 167-169.
- Kryukov, P.A., 1961. Toward procedures of squeezing out of solutions from sedimentary rocks. *Gidrokhim. Inst. Novochoerkask., Gidrokhim. Mater.*, 33: 191-197.
- Kryukov, P.A., 1964. Soil, Mud and Rock Solutions (Diss. Abs.). Akad. Nauk S.S.S.R., Inst. Geochemistry and Anal. Chem. of V.I. Vernadskiy, Moscow, 56 pp.
- Kryukov, P.A., Komarova, N.A., 1954. On squeezing fluids from clays at very high pressures (Russ.). *Dokl. Akad. Nauk S.S.S.R.*, 99(4): 617-619.
- Lambe T.W., Whitman, R.V., 1969. *Soil Mechanics*. John Wiley & Sons, Inc., New York, 553 pp.
- Langmuir, D., 1997. *Aqueous Environmental Geochemistry*. Prentice Hall, 600 pp.
- Lipman, C. P., 1918. A new method of extracting the soil solution. University of California. *Publ. on Agricultural Science*, 3, 131-134.
- Low, P.F., 1976. Viscosity of Interlayer Water in Montmorillonite. *Soil Sci. Soc. Am. J.* 40, 500–505
- Low, P.F., 1976. Viscosity of Interlayer Water in Montmorillonite. *Soil Sci. Soc. Am. J.* 40, 500–505.
- Luszczynski, N.J., 1961. Filter-press method of extracting water samples for chloride analysis. US Geological Surv. Water supply paper 1544-A, 1-8.
- Lutz, J.F., Kemper, W.D., 1959. Intrinsic permeability of clay as affected by clay-water interaction. *Soil Science* 88, 83-90.
- Mäder, U. K., Waber, H.N., Gautschi, A., 2004. New method for pore water extraction from claystone and determination of transport properties with results for Opalinus Clay (Switzerland). *Proceedings of the Eleventh International Water-Rock Interaction Conference, Saratoga Springs, New York*, pp. 445-449.
- Mangelsdorf, P.C., Wilson, T.R.S., Daniell, E., 1969. Potassium enrichments in interstitial waters of recent marine sediments. *Science* 165, 171-174.
- Manheim, F.T. and Sayles, F.L., 1974. Composition and origin of interstitial waters of marine sediments, based on Deep Sea Drill cores. In Goldberg, E.D. (Ed.), *The sea*, v. 5: New York (John Wiley & Sons), p. 527-568.
- Manheim, F.T., 1966. A hydraulic squeezer for obtaining interstitial waters from consolidated and unconsolidated sediments. USGS Prof. Paper 550C, pp. C256-C261.
- Manheim, F.T., 1974. Comparative studies on extraction of sediment interstitial waters: discussion and comment on the current state of interstitial water studies. *Clay and Clays Minerals*, 22, 337-343.
- Manheim, F.T., Bischoff, J.L., 1969. Geochemistry of pore waters from shell oil company drillholes on the continental slope of the northern Gulf of Mexico. *Chem. Geol.* 4, 63-82.
- Manheim, F.T., Brooks, E.G., Winters, W., 1994. Description of a hydraulic sediment squeezer. U.S. Geological Survey. Open-File Report 94-584.

- Manheim, F.T., Sayles, F.L., 1974. Composition and origin of interstitial waters of marine sediments, based on Deep Sea Drill cores. In Goldberg, E.D. (Ed.), *The sea*, v. 5: New York (John Wiley & Sons), p. 527-568.
- Masuzawa, T., Kanamori, S., Kitano, Y., 1980. The reversible effect of temperature on the chemical composition of interstitial water of marine sediment. *Journal of the Oceanographical Society of Japan* 36, 68-72.
- Mazurek, M., Alt-Epping, P., Bath, A., Gimmi, T., Waber, H.N., 2009. Natural Tracer Profiles across argillaceous formations: The CLAYTRAC project. NEA No. 6253, *Radioactive Waste Management*. OECD publishing, Paris, 361 pp.
- Mazurek, M., Waber, H.N., Oyama, T., Külls, C., 2012. Characterization of pore water in compacted shales and marls by squeezing experiments at 200-500 MPa. *Clays in Natural and Engineered Barriers for Radioactive Waste Confinement*. 5th International meeting Mont Pellier 2012. Abstract Book pp. 401-402.
- McKelvey, J.G. and Milne, I.H., 1962. Flow of salt solutions through compacted clay. *Clays Clay Miner. Proc. Natl. Conf. Clays Clay Miner.* 9 (1960), 248-259.
- Michelot, J.L., Ricard, P., Barbreau, A., Boisson, J.Y., 1995. Environmental isotope study of pore water and of fracture calcites in the Tournemire Toarcian Claystones: Sampling, Analyses, and preliminary interpretation. In: *Proceedings of and International Workshop on Hydraulic and Hydrochemical Characterisation of Argillaceous Rocks*. 7-9 June 1994 Nottingham, UK. OECD/NEA documents, Paris, pp. 133-136.
- Millero, F.J., 1982. The effect of pressure on the solubility of minerals in water and sea water. *Geochim. Cosmochim. Acta*. Vol 48, pp. 571-81.
- Morgan, J.F., 1916. The soil solution obtained by the oil pressure method. *Mich. Agric. Exp. Sta. Tech. Bull.* 28, pp. 1-38.
- Morgenstern, N.R., and Balasubramanian, B.I., 1980. Effects of pore fluid on the swelling of clay shale. In: *Proceedings of the Fourth International Conference on Expansive Soils, Characterization and Treatment of Expansive Soils for Engineering Design*. American Society of Civil Engineers, New York, 4, 190-205.
- Mower, I.E., Higgins, J.D., Yang, I.C., and Peters, C.A., 1994. Pore-water extraction from unsaturated tuff by triaxial and one-dimensional compression methods, Nevada Test Site: U.S. Geological Survey Water-Resources Investigations Report 93-4144, 79 p.
- Mower, T.E., Higgins, J.D., Yang, I.C., and Peters, C.A., 1994. Pore-water extraction from unsaturated tuff by triaxial and one-dimensional compression methods, Nevada Test Site: U.S. Geological Survey Water-Resources Investigations Report 93-4144, 79 p.
- Mudroch, A., Rosa, F., Reynoldson, T., Hall, G., Kezhum, Z., Coker, R., 1994. Effects of subaqueous gold mine tailings on Larder Lake ecosystems, National Water Research Inst, Contribution 94-03.
- Murray, J., Irvine, R., 1985. On the chemical changes which take place in the composition of the sea water associated with blue muds on the floor of the ocean. *Trans. Royal Soc. Edinburgh*, 37, 481-507.
- Murray, J.W., Emerson, S., Jahnke, R., 1980. Carbonate caption and the effect of pressure on the alkalinity of interstitial waters from the Guatemala Basin. *Geochimica et Cosmochimica Acta* 44, 963- 972.
- Murthy, A.S.P and Ferrel, R.E., Jr., 1972. Comparative chemical composition of sediment interstitial waters. *Clay Miner*, 20, pp 317-321.
- Muurinen, A., 1994. Diffusion of anions and cations in compacted sodium bentonite. Technical research centre of Finland. VTT publications 168, 75 pp.

- Muurinen, A., Carlsson, T., 2007. Development of methods for on-line measurements of chemical conditions in compacted bentonite. *Physics and Chemistry of the Earth*, 32, 241-246.
- Muurinen, A., Lehtikoinen, J., 1999. Pore water chemistry in compacted bentonite. *Engineering Geology*, 54, pp. 207-214.
- Nagra, 2002. Project Opalinus Clay, Demonstration of disposal feasibility for spent fuel, vitrified high-level waste and long-lived intermediate-level waste, Safety Report, Technical report 02-05.
- Northrup, Z., 1918. The true soil solution. *Science* 47, 638-639.
- Ondraf-Niras, 2001. SAFIR 2 Report, Safety Assessment and Feasibility Interim Report 2; coordinated by De Preter P., Lalieux P. and Cool W. (eds.). Ondraf-Niras, Belgian Agency for Radioactive Waste and Enriched Fissile Materials., four volumes, 13 chapters; NIROND 2001-06 E, December 2001, 570 pp.
- Parkhurst D.L., Appelo C.A.J., 1999. PHREEQC2 - A computer program for speciation reactionpath, 1D-Transport and inverse geochemical calculations. U.S. Geological Survey.
- Patterson, R.J., Frape, S.K., Dykes, L.S., McLeod, R.A., 1978. A coring and squeezing technique fro the detailed study of subsurface chemistry. *Can. J. of Earth Sci.*, 15-162-169.
- Pearson, F.J., 1998. Geochemical and other porosity types in clay-rich rocks. *Water-Rock interaction*, Arehart & Hulston (eds.), pp. 259-262. Balkema. Rotterdam.
- Pearson, F.J., Arcos, D., Bath, A., Boisson, J. Y., Fernández, A.M^a, Gäbler, H-E, Gaucher, E., Gautschi, A., Griffault, L., Hernán, P., Waber, H.N., 2003. Geochemistry of water in the Opalinus Clay Formation at the Mont Terri Rock Laboratory. *Swiss Federal Office for Water and Geology Series*, N° 5, 319 pp.
- Pearson, F.J., Fernández, A.M^a, Gaboriau, H., Waber, H.N., Bath, A., 2003b. Annex 10. Porosity and water content of Mont Terri Claystones. In: Pearson et al., 2003. *Geochemistry of water in the Opalinus Clay Formation at the Mont Terri Rock Laboratory*. Swiss Federal Office for Water and Geology Series, N° 5, pp. 304-319.
- Pearson, F.J., Tournassat, C., Gaucher, E., 2011. Biogeochemical processes in a clay formation in-situ experiment: Part E. Equilibrium controls on chemistry of pore water from the Opalinus Clay, Mont Terri underground research laboratory, Switzerland. *Applied Geochemistry* 26, 990-1008.
- Peters, C. A., Yang, Y. C., Higgins, J. D., Burger, P. A., 1992. A preliminary study of the chemistry of pore water extracted from tuff by one-dimensional compression. *Water-Rock Interaction*, Kharaka & Maest (eds.), pp. 741-745.
- Poinssot C., Baeyens B. and Bradbury M.H., 1999. Experimental and modelling studies of caesium sorption on illite. *Geochimica et Cosmochimica Acta*, 63, 3217-3227.
- Presley, B.J., Brooks, R.R. and Kappel, H.M., 1967. A simple squeezer for removal of interstitial water from ocean sediments. *J. Mar. Res. (Sears Found. Mar. Res.)*, 25(3), 355-357.
- Pusch, R., Muurinen, A., Lehtikoinen, J., Bors, J., Eriksen, T., 1999. Microstructural and chemical parameters of bentonite as determinants of waste isolation efficiency. European Commission. Nuclear Science and Technology. Project Report EUR 18950 EN.
- Ramann, E., Marz, S., Bauer, H., 1916. Uber boden-press-säfte. *Int. Mitt. Für Bodenkunde*, 6(1), 27-34.
- Reeburgh, W.S., 1967. An improved interstitial water sampler. *Limnol. Oceanogr.* 12: 163-165.
- Reeder, S., Cave, M.R., Entwisle, D.C., Trick, J.K., 1998. Extraction of water and solutes from clayey material: a review and critical discussion of available techniques. British Geological Survey. Technical Report WI/98/4C, 60 pp.
- Richards, L.A., 1941. A pressure-membrane extraction apparatus for soil solution. *Soil Sci.* 51, 377-386.

- Ridout, P.S., 1981. A shipborne system for extracting interstitial water from deep ocean sediments., IOS. Rep., 121, pp 13.
- Rieke III, H.H., Chilingarian, G.V., 1974. Compaction of Argillaceous Sediments. *Developments in Sedimentology*, 16. Elsevier, Amsterdam, 424 pp.
- Rieke III, H.H., Ghose, S.K., Fahhad, S.A. and Chilingar, G.V., 1969. Some data on compressibility of various clays. *Int. Clay Con\$, Tokyo, Japan*, 1: 817-828.
- Rosenbaum, M.S., 1976. Effect of compaction on the pore fluid. *Clays and Clay Minerals* 24, 118-121.
- Ross, C.A.M., Bath, A.H., Entwisle, D.C., Cave, M.R., Fry, M.B., Green, K.A., Reeder, S., 1989. Hydrochemistry of porewaters from Jurassic Oxford Clay, Kellaways Beds, Upper Estuarine and Upper Lias formations at the Elstow site, Bedfordshire. Nirex Safety Studies Research Report NSS/R172. UK Nirex Ltd.
- Sacchi, E., Michelot J.L., 2000. Porewater extraction from argillaceous rocks for geochemical characterization: Methods and Critical Evaluation. Report prepared for the OECD/NEA "Clay Club". OECD, Paris. 185 pp.
- Sacchi, E., Michelot, J.L., Pitsch, H., Lalieux, P. and Aranyosy, J.F., 2001. Extraction of water and solution from argillaceous rock for geochemical characterisation: Methods, processes, and current understanding. *Journal of Hydrogeology*, 9, pp. 17-33.
- Sage, B.H., Schaafsma, J.G. and Lacey, W.N., 1934. Phase equilibria in hydrocarbon systems, V. Pressure-volume-temperature relations and thermal properties of propane. *Ind. Eng. Chem.*, 26(11): 1218-1224.
- Sasseville, D.R., Takacs, A.P., Norton, S.A., Dabis, R.B., 1974. A large-volume interstitial water sediment squeezer for lake sediment. *Limnol. Oceanogr.*, 19, 1001-1004.
- Sawabini, C.T., Chilingar, G.V. and Allen, D.R., 1971. Design and operation of a triaxial, high-pressure compaction apparatus. *J. Sediment. PetroL*, 41(3): 871-881.
- Sawhney, B. L., 1970. Potassium and cesium ion selectivity in relation to clay mineral microstructure. *Clays Clay Miner.* 18, 47-52.
- Sayles, F. L., Wilson, T. R. S., Hume, D. N., Mangelsdorf, P. C. Jr., 1973. In situ sampler for marine sedimentary pore waters: evidence for potassium depletion and calcium enrichment, *Science* 181, 154-156.
- Sayles, F.L., 1970. Preliminary geochemistry. In R.G. Bader et al. (Eds.). *Initial reports Deep Sea Drilling Project*. Washington. U.S. Gov. Printing Office, pp. 645-655.
- Sayles, F.L., 1979. The composition and diagenesis of interstitial solutions. I. Fluxes across the seawater--sediment interface in the Atlantic Ocean. *Geochimica et Cosmochimica Acta*, 43, 527-545.
- Shen, Z., Tang, M., 1992. Research on pore solution chemistry and environmental significance. *Water-Rock Interaction*, Kharaka & Maest (eds.), pp. 427-431.
- Shepard, F.P. and Moore, D.G., 1955. Central Texas Coast sedimentation. *Bull. Am. Assoc. Pet. Geologists*, 39, 1463-1593.
- Shishkina, O.V. and Tsvetkov, G.A., 1978. Separation of interstitial waters using a cooling system *Oceanology.*, 18, pp 428-430.
- Shishkina, O.V., 1968. Methods of investigating marine and ocean waters. In: G.V. Bogomolov et al. (Editors), *Pore Solutions and Methods of Their Study - A Symposium*. Izd. Nauka i Tekhnika, Minsk, pp. 167-176.
- Shishkina, O.V., 1972. *Geokhimiya morskikh i okeanicheskikh ilovykh vod.* (Geochemistry of marine and ocean pore fluids). Moscow: Izdat. Nauka, p. 227.

- Sholkovitz, E., 1973. Interstitial water chemistry of the Santa Barbara Basin sediments. *Geochim. Cosmochim. Acta.*, 37, pp 2043- 2073.
- Sholl, D.W., 1963. Techniques for removing interstitial water from coarse-grained sediments for chemical analysis. *Sedimentol.* 2, 156-163.
- Siever, R., 1962. A squeezer for extracting interstitial water from modern sediments. *J. Sediment. Petrol.*, 32(2), 329-331.
- Siever, R., Beck, K.C., Berner, R.A., 1965. Composition of interstitial waters of modern sediments. *Journal of Geology* 73, 39-73.
- Standing, M.B., 1952. *Volumetric and Phase Behavior of Oil Field Hydrocarbon Systems*. Reinhold, New York, N.Y., 122 pp.
- Terzaghi, K., 1925. *Erdbaumechanik auf bodenphysikalischer Grundlage*. Deuticke, Leipzig, 399 pp.
- Thury, M., Bossart, P., 1999. Mont Terri Rock Laboratory. Results of the Hydrogeological, Geochemical and Geotechnical Experiments Performed in 1996 and 1997. *Geol. Rep. Swiss natl. Hydrol. Geol. Surv.* 23, 191 pp.
- Tournassat, C., Lerouge, C., Blanc, P., Brendle, J., Greneche, J.M., Touzelet, S., Gaucher, E.C., 2008. Cation exchanged Fe(II) and Sr compared to other divalent cations (Ca, Mg) in the Bure Callovian-Oxfordian formation: Implications for pore water composition modelling. *Applied Geochemistry* 23, 641-654.
- Troup, B.N., Bricker, O.P., Bray, J.T., 1974. Oxidation effect on the analysis of iron in the interstitial water of anoxic sediments. *Nature* 249, 237.
- Van der Knaap, W. and Van der Vlis, A.C., 1967. On the cause of subsidence in oil-producing areas. *Proc. 7th World Pet. Congr.*, Mexico City, Mexico. Elsevier, Amsterdam, 3: 85-95.
- Van Loon, L.R., Soler, J.M., Bradbury, M.H., 2003. Diffusion of HTO, ³⁶Cl⁻ and ¹²⁵I⁻ on Opalinus clay samples from Mont Terri—effect of confining pressure. *J. Contam. Hydrol.* 61, 71–83.
- Vinsot A., Appelo C.A.J., Cailteau C., Wechner S., Pironon J., De Donato P., De Cannière P., Mettler S., Wersin P., Gäbler H.E., 2008. CO₂ data on gas and pore water sampled in situ in the Opalinus Clay at the Mont Terri rock laboratory. *Physics and Chemistry of the Earth* 33, S54-S60.
- Vinsot A., Mettler S. and Wechner S., 2008. In situ characterization of the Callovo-Oxfordian pore water composition. *Phys. Chem. Earth* 33, S75–S86.
- Von Engelhardt, W. and Gaida, K.H., 1963. Concentration changes of pore solutions during the compaction of clay sediments. *J. Sediment. Petrol.*, 33(4): 919-930.
- Waber, H.N., Gaucher, E., Fernández, A.M., Bath, A., 2003. Annex 3: Aqueous Leachates and cation exchange properties of Mont Terri Claystones. In: Pearson et al., 2003. *Geochemistry of Water in the Opalinus Clay Formation at the Mont Terri Rock Laboratory*. FOWG N° 5, pp. 200-237.
- Wersin, P., Leupin, O.X., Mettler, S., Gaucher, E.C., Mäder, U., De Canniere, P., Vinsot, A., Gäbler, H.E., Kunimaro, T., Kiho, K., Eichinge, L., 2011. Biogeochemical processes in a clay formation in situ experiment: Part A – Overview, experimental design and water data of an experiment in the Opalinus Clay at the Mont Terri Underground Research Laboratory, Switzerland. *Applied Geochemistry*, 26, 931-953.
- Yang, I.C., Turner, A.K., Sayre, T.M., and Montazer, P., 1988, Triaxial-compression extraction of pore water from unsaturated tuff, Yucca Mountain, Nevada: U.S. Geological Survey Water-Resources Investigations Report 88-189, 68 p.

Yang, L.C., Higgins, J.D., Hayes, L.R., 1995. Porewater extraction from unsaturated tuff using triaxial and one-dimensional compression methods. Proc. of an Int. Workshop on Hydraulic and hydrochemical characterisation of argillaceous rocks, Nottingham, U.K., 7-9 June 1994, OECD/NEA, pp. 137-155.

Yong, R.N., Warkentin, B.P., 1975. Soil properties and behavior. Elsevier, Amsterdam, 449 pp.

Annex A. Squeezing devices used over time

Annex A.1. Low Pressure Squeezing apparatus

- Designed to extract water from high moisture content materials (40-70%)
- Marine and lacustrine sediments or unconsolidated sediments
- Squeezing pressures: 1.5 to 30 MPa

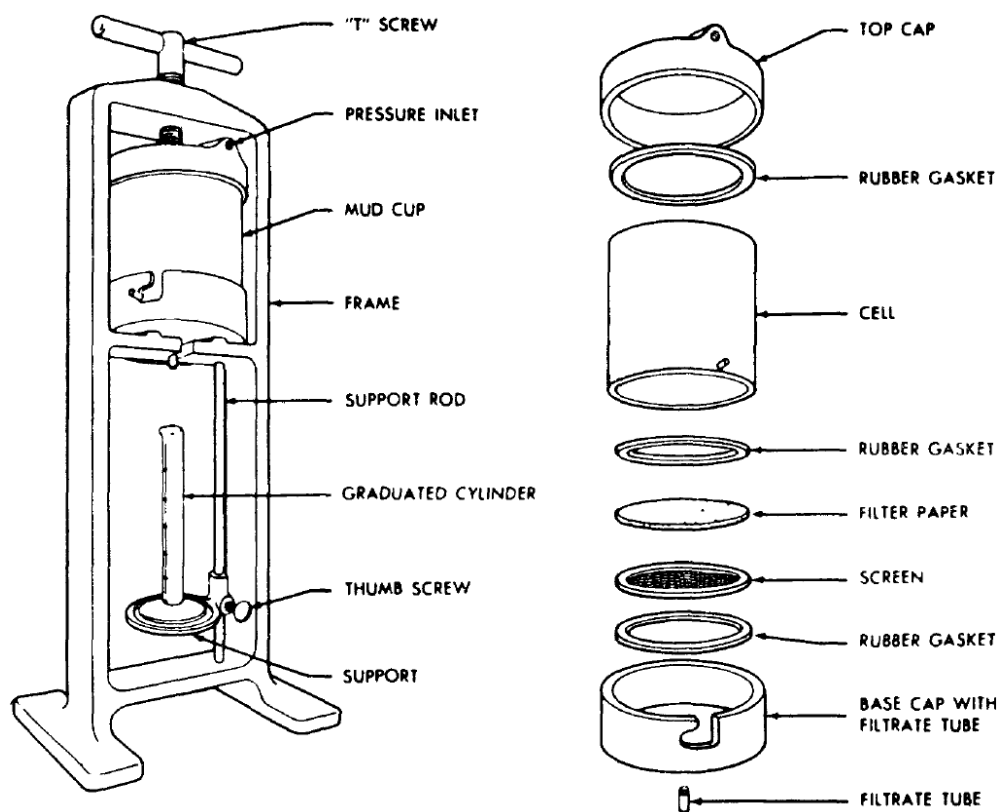


Figure A- 1. Filter press and chamber assembly. Courtesy of Bariod Division, National Lead Co. Luszczynski (1961)

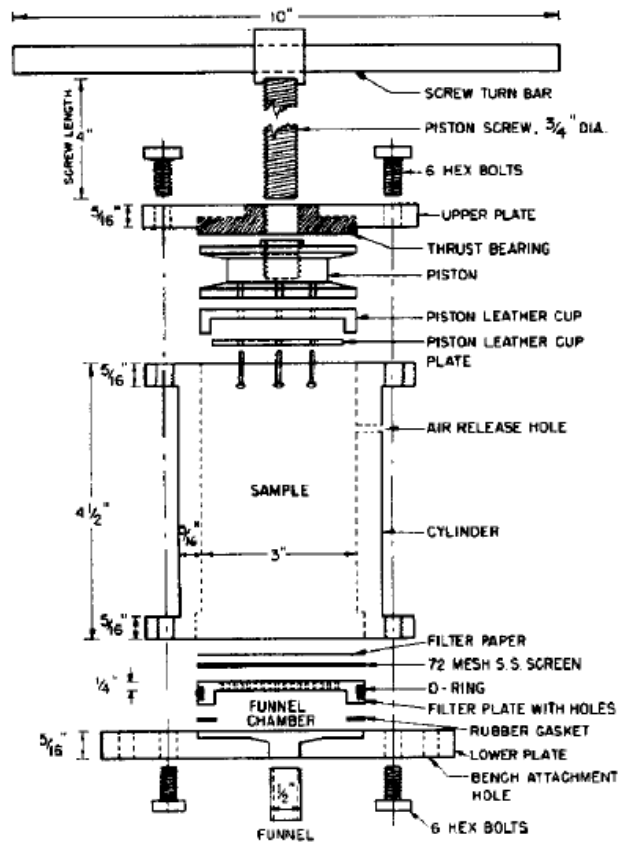


Figure A- 2. Exploded drawing of sediment squeezer. Siever (1961)

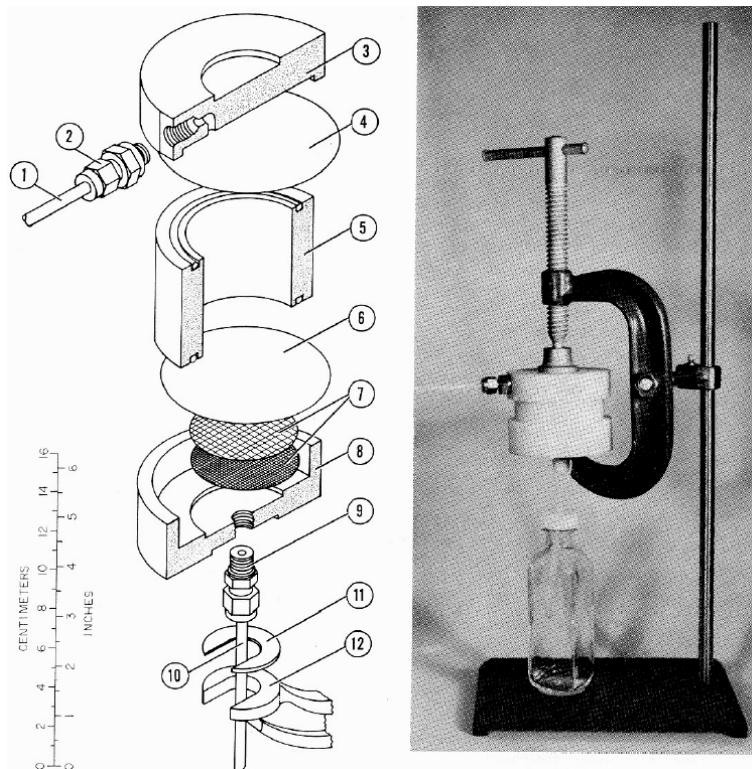


Figure A- 3. Exploded isometric drawing of squeezer and a photograph: 1) nylon gas inlet tube, 2) O-ring seal male plug (Swagelok), 3) Delrin cap, 4) dental dam rubber diaphragm, 5) nylon sample retainer with O-rings, 6) filter, 7) nylon screens, 8) Delrin base, 9) nylon male plug (Swagelok), 10) nylon sample drain tube, 11) rubber or cork pad, and 12) modified C-clamp. 1.4 MPa (Gas-mechanical action), 25 mL/100 g sample, 30 to 45 min. operation. Reeburgh (1967)

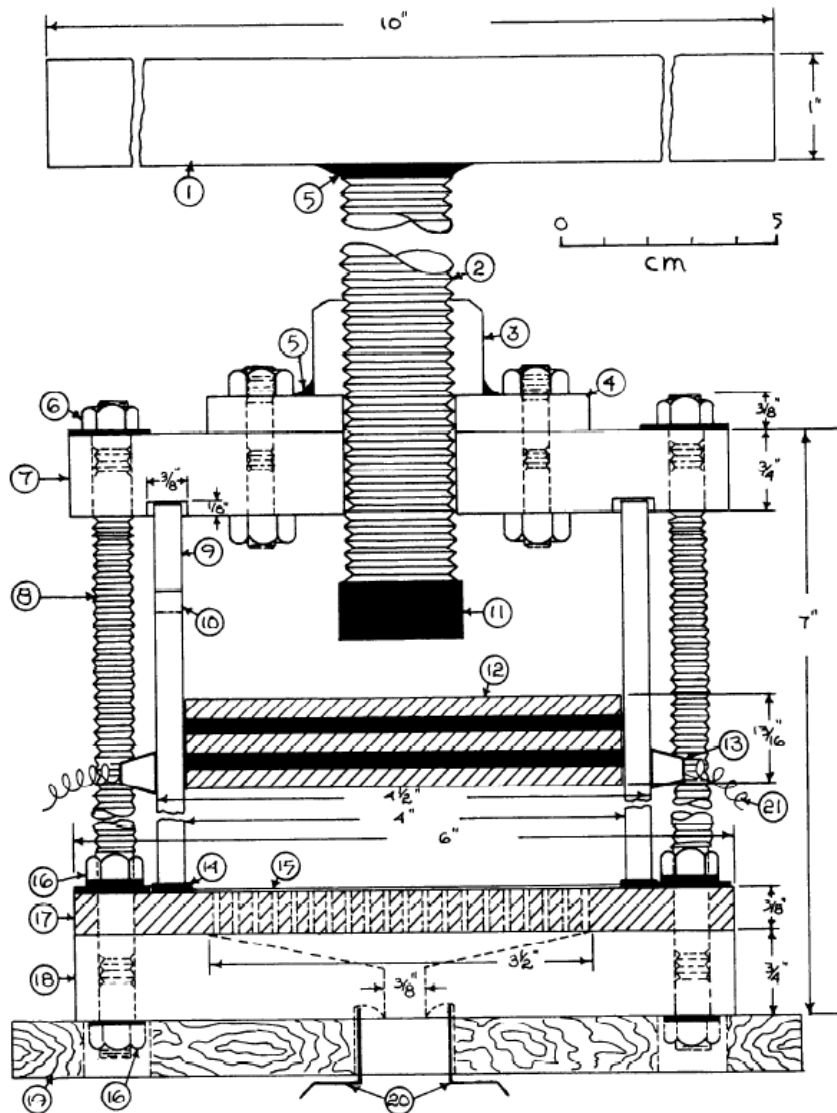


Figure A- 4. Cutaway view of sediment squeezer: 1) Galvanized pipe, 2) threaded rod (23 cm long), 3) bolt to match 2, 4) iron plate, 5) weld between 1 and 2 and between 3 and 4. The above five items are all coated with a clear acrylic spray (Crylon), 6) Hex nut and flat washer, 7) aluminium top plate, coated. Parts 1,2,3,4 and 7 are permanently assembled. 8) Threaded rod, 9) PVC tubing, lathed square on top and bottom, 10) air hole, 11) Plastic cap to prevent abrasion of Teflon piston, 12) Teflon piston with two neoprene O-rings. The clearance between the piston and the PVC wall should be just enough to allow the piston to be forced by hand through the cylinder with the O-rings not in place and no lubricant. Pistons should be mated to cylinders because of variation in the diameter and shape of PVC tubes. 13) Countersunk steel band around PVC wall with provisions for attaching a spring to the band, 14) Neoprene nonpermeable gasket, 15. Whatman No. 50 filter paper (2 sheets), 12.5 cm., 16) Hex nut, lock washer and flat washer, 17. Perforated Teflon baseplate, 18. Aluminium base with drainage surface and exit hole, coated with clear acrylic spray (or Teflon base). Parts 8, 16, 17 and 18 are permanently assembled., 19) squeezer board, drilled to accept 8, 20) Polyethylene 125-mL narrowmouth bottle, 21) Springs with attach from band to eyebolt on squeezer board.

Sasseville et al. (1974)

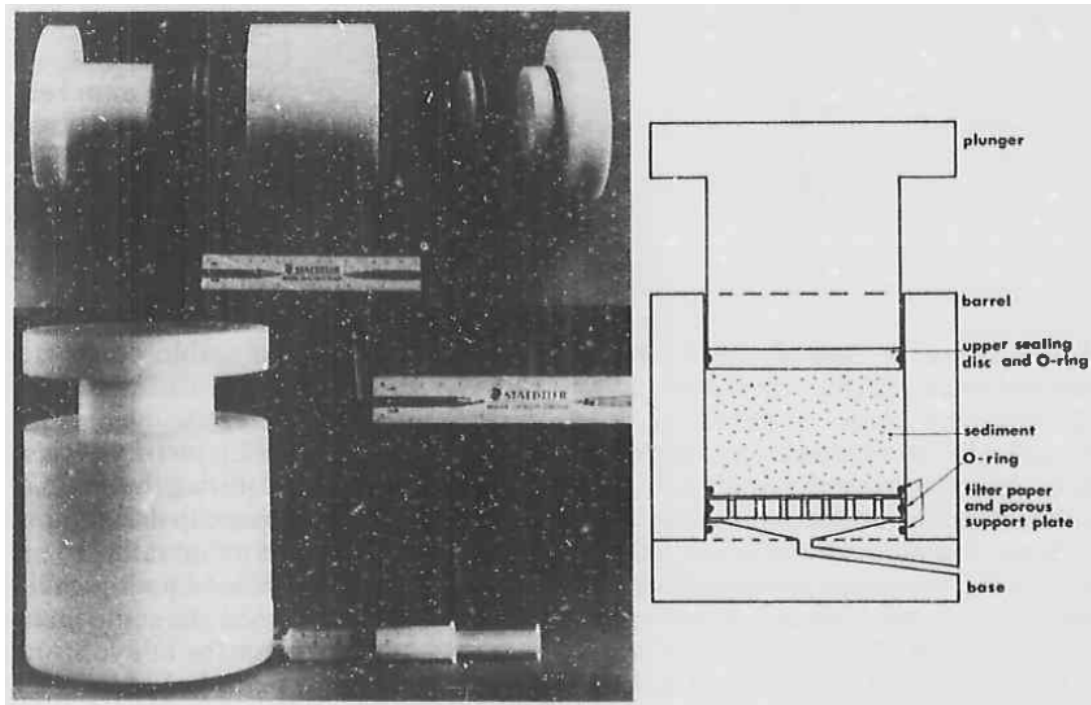


Figure A- 5. Mechanical Delrin squeezer. Right: Exploded view of squeezer; Upper Left: from the left to the right the parts are: plunger, upper sealing disc barrel, O-ring to secure filter paper, porous support plate and base. Lower Left: Assembled squeezer with syringe in place. Patterson et al. (1978)

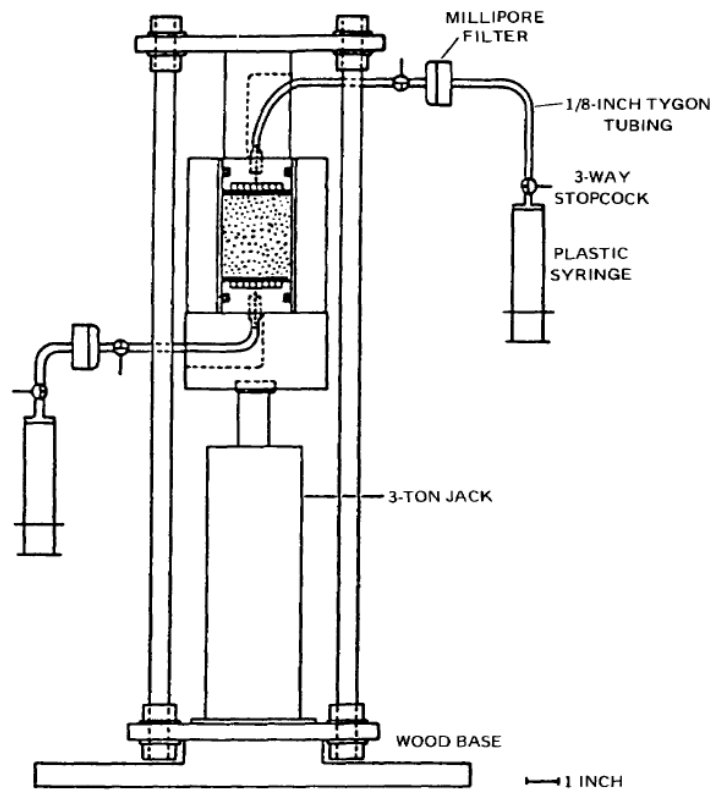


Figure A- 6. Design of a sediment squeezer (Kalil and Goldhaber, 1973)

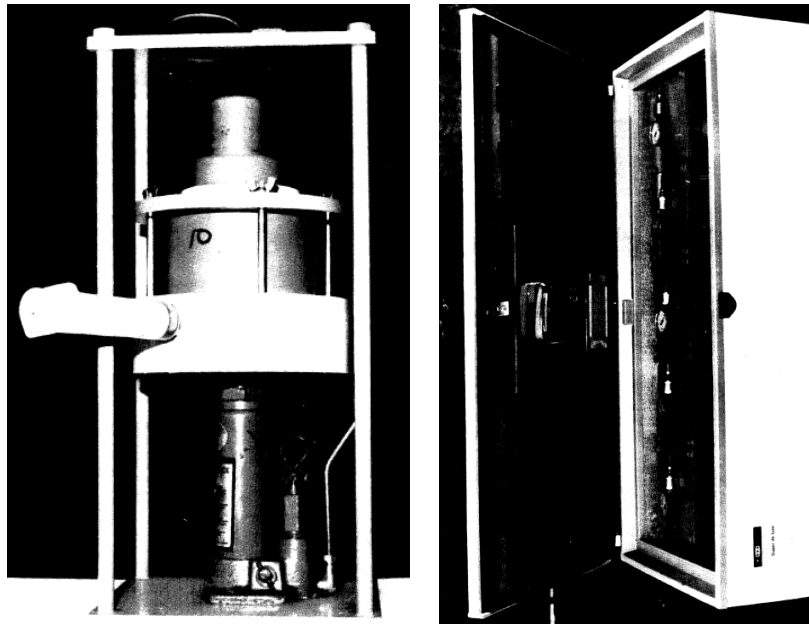


Figure A- 7. Sediment squeezing unit and squeezing unit fixed in a cooler cabinet. Shipboard System, 14-28 MPa (Hydraulic jacks), 25 mL/100 g sample, 30 min. operation. Ridout (1981)

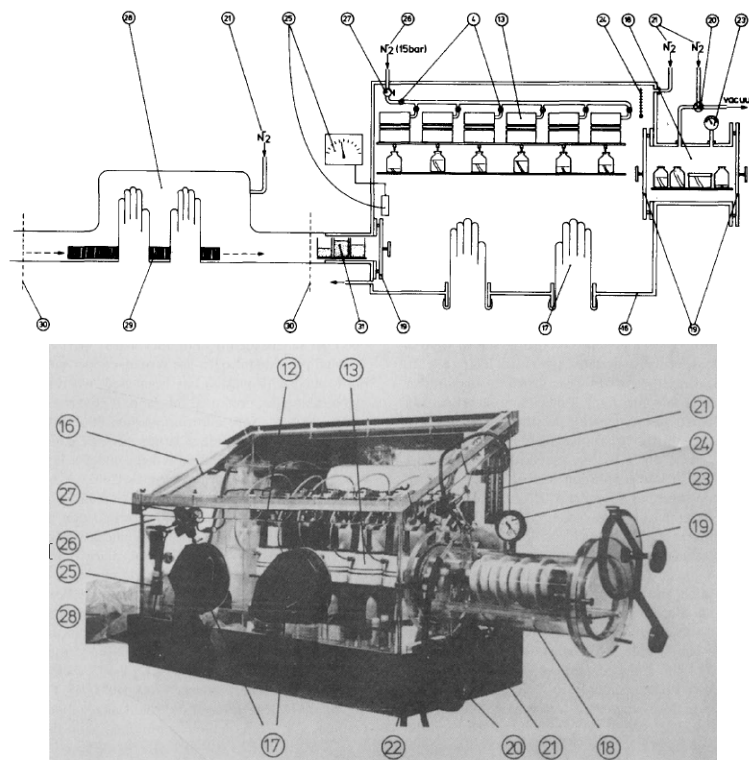


Figure A- 8. Hydraulic Schematic representation of the shipboard pore water extraction system (arbitrary scale): 12) Three-way cock (Whitey 43XS4), 13) Squeezer, 16) Glove box made of 10 mm Perspex, 17) Neoprene gloves (Labconco), 18) Large sluice, 19) Sluice door, 20) Three-way cock (Whitey 44XS10mm), permitting either nitrogen influx to the sluice or the creation of vacuum in the sluice, 21) Low-pressure high purity nitrogen tubing (oxygen less than 0.0005%), 23) Manometer; 24) Thermometer (min/max), 25) Oxygen probe, 26) High pressure nitrogen tubing (oxygen less than 0.0005%), 27) Pressure regulator, 28) Glove bag (I2R, both sides extended with polyethylene tubing), 29) split core section, 30) Quick-closing clamps, 31) Polyethylene beakers with samples for pore-water extraction. Glove box made of Delrin. de Lange (1992)

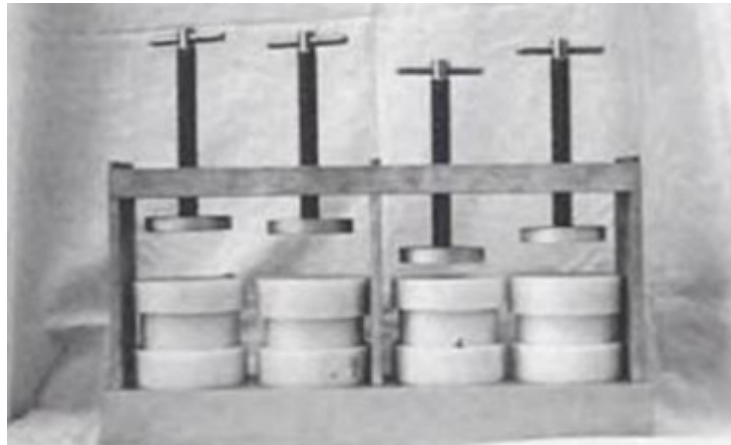


Figure A- 9. Multiple clamping devices for sediment squeezing (“Quad-Clamp”): 1.4 MPa, 25 mL/100g, 30-45 min. operation (Rosa and Davis, 1993)

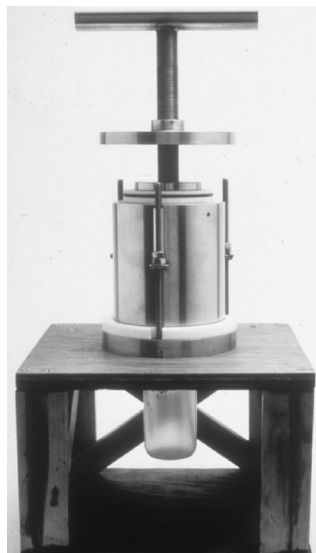


Figure A- 10. Sediment squeezing apparatus for extracting interstitial water. Photo courtesy of Allen Burton. EPA Methods for collection, storage and manipulation of sediments for chemical and toxicological analyses: Technical Manual (2001)

Annex A.2. High Pressure Squeezing Systems

- Designed to extract water from low moisture content materials (5-30%)
- Bentonites, consolidated and indurated clayrocks and concrete
- Squeezing pressures: 10 MPa to 600 MPa

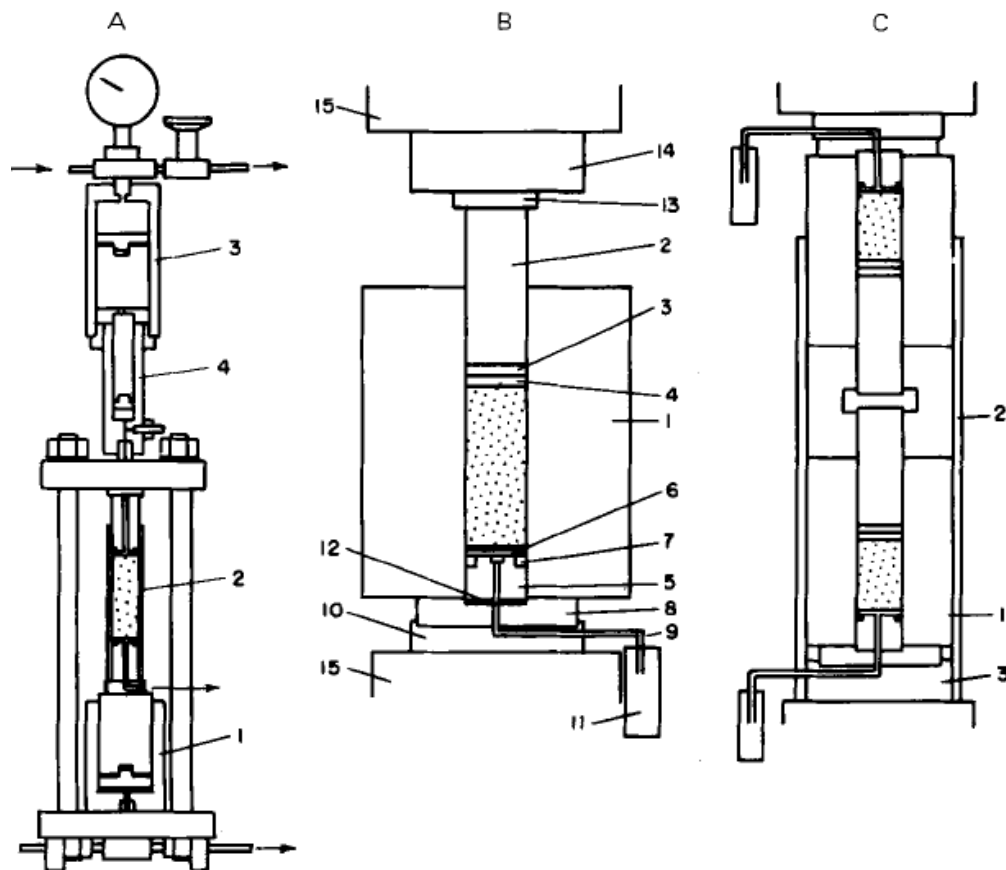


Figure A- 11. Various high-pressure apparatuses used by Kryukov and his associates. A) Schematic diagram of apparatus for replacement of solutions, B) Apparatus for squeezing out of solutions at pressures up to 10,000 kg/cm², and C) Schematic diagram of a duplex apparatus for squeezing out interstitial solutions (After Kryukov, 1961)

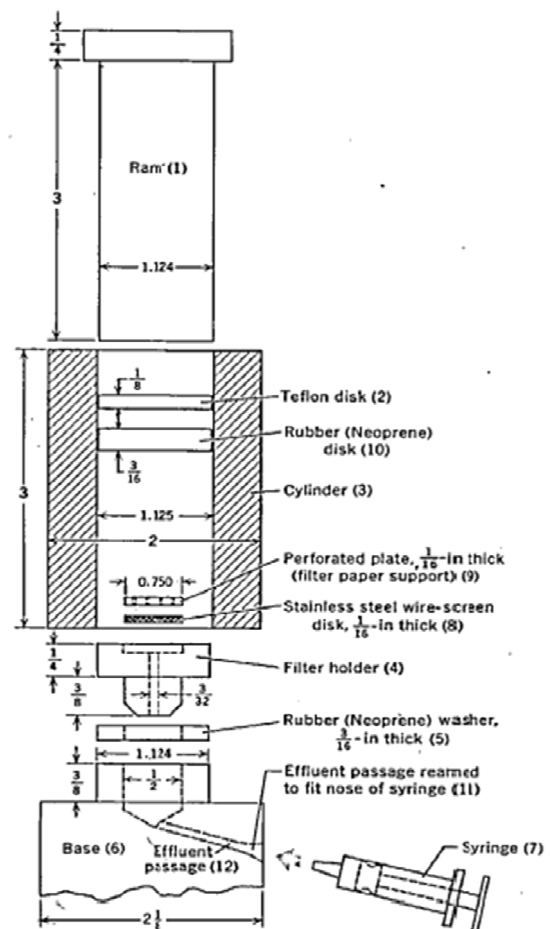
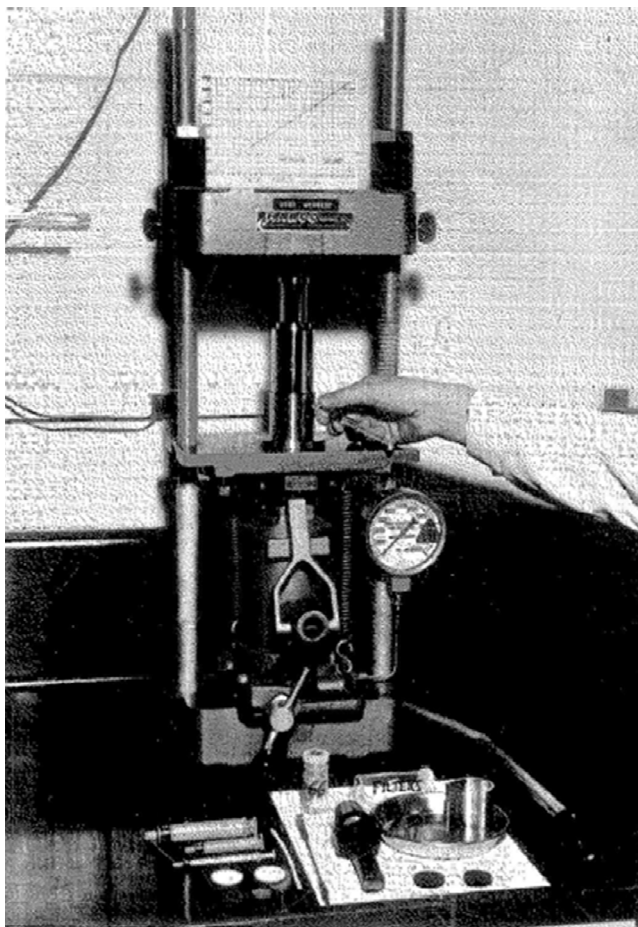


Figure A- 12. Hydraulic squeezer set up for operation and drawing showing components of hydraulic squeezer. All dimensions in inches. Base is about 2½ inches in height. The accessories on the bench include the following: several sizes of disposable syringes, perforated plate, Teflon and rubber gaskets, filter disks, arbor punch, and half-round steel holder. The half-round holder is used to support the squeezer while the sediment plug and filter plate are being pushed out of the piston after extraction is completed. The arbor punch is used to punch out rubber and Teflon gaskets and filter-paper disks. Manheim (1966).



Figure A- 13. A) Hydraulic squeezer set-up for operation used during the Deep Sea Drilling Project, B) Squeezer capsule, disposable syringe and spacer block positioned, C) Squeezer capsule components and accessory parts accompanied by three compressed sediment discs, and D) Stainless steel squeezer capsules used to extract pore fluid from sediments. Left: model A (smallest capsule) used on stiff fine-grained or coarse-grained sediments. Right: model B (largest capsule) used on softer finer-grained sediments. 34-138 MPa, 10-50 cm³ sample, 10-50 mL water, 10 min. operation. Manheim et al. (1994)

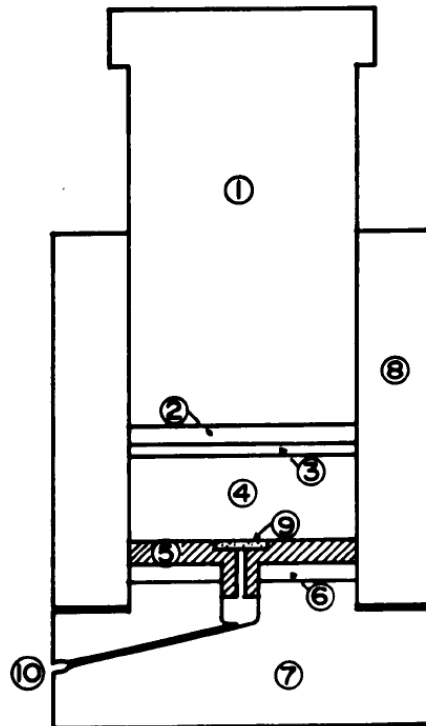


Figure A- 14. Pore water squeezer: 1) Steel piston with chromium plating, 2) Rubber disc, 3) Teflon disc, 4) Soil sample, 5) Stainless steel disc, 6) Rubber ring, 7) Base-Stainless steel, 8) Stainless steel cylinder, 9) Porous Nickel, 10) Pore water outlet. Connection for syringe. Scale: Half size. Iyer (1990); Morgenstern et al. (1980)

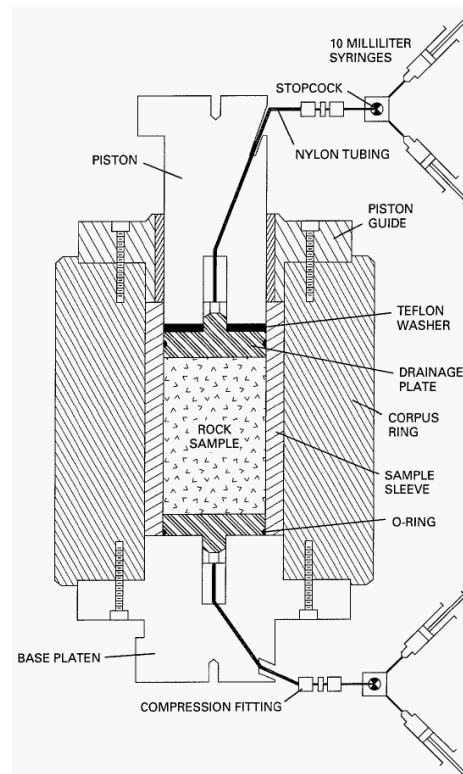
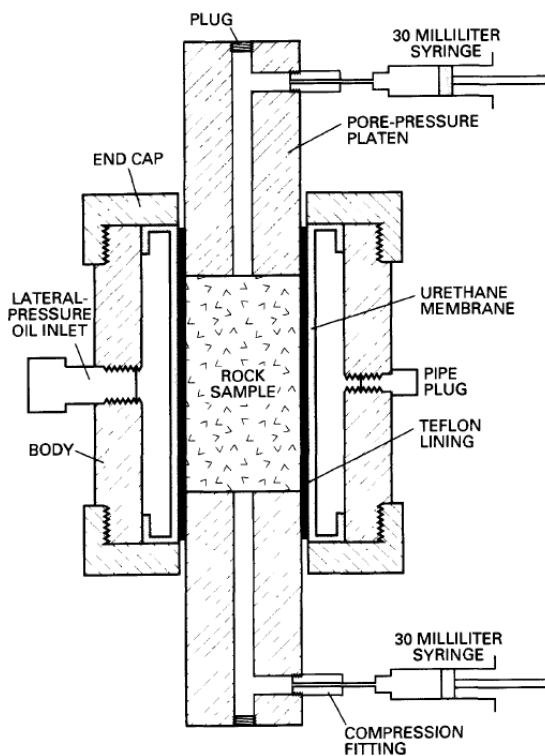


Figure A- 15. Triaxial cells for pore water extraction. a) Triaxial cell used by Yang et al. (1988), and b) Modified triaxial cell (one-dimensional compression cell) used by Mower et al. (1994) and Peters et al. (1992). Unsaturated tuffs at Yucca Mountain, 68 MPa, 3 mL water, 6.1 cm ϕ /10 cm high, 6-8 hours operation

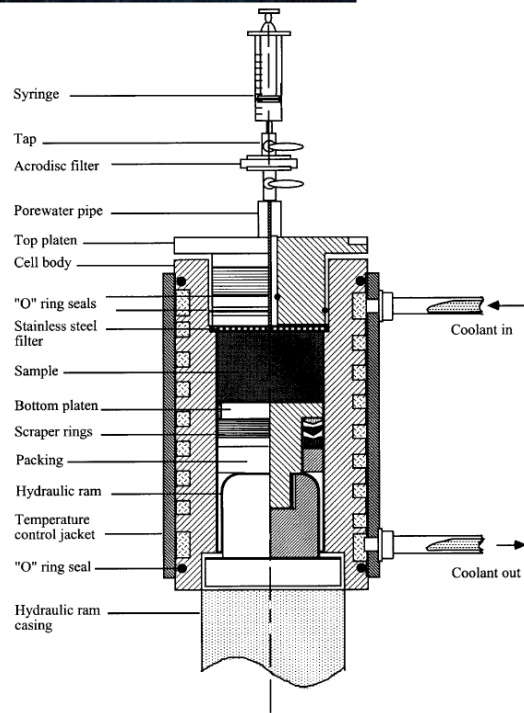
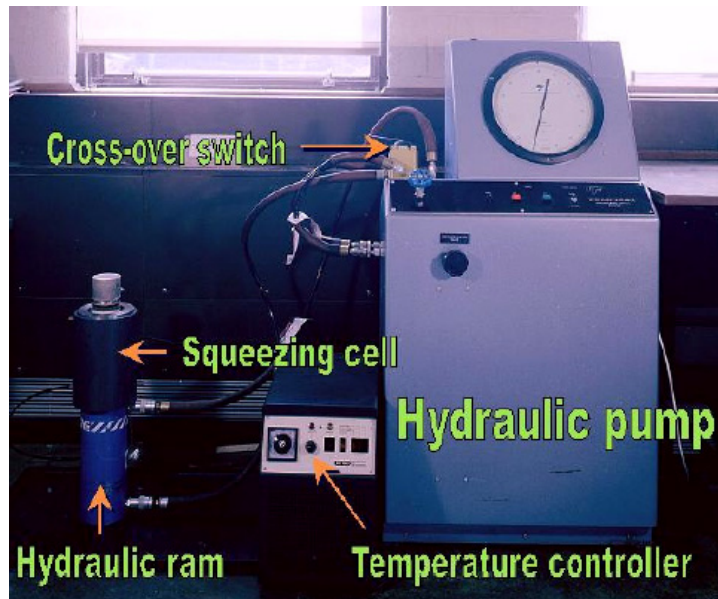


Figure A- 16. Squeezing apparatus and clay squeezing cell, designed and manufactured by R&D Workshop, BGS Keyworth. Entwistle and Reeder (1993), Di Bonito et al. (2008)

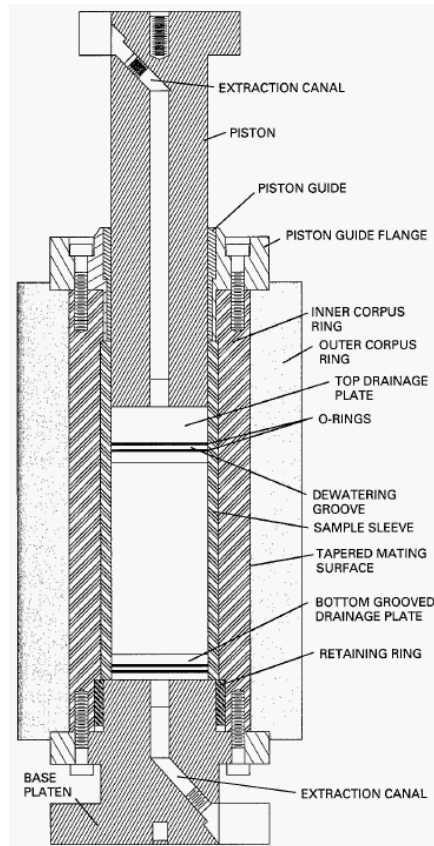


Figure A- 17. High-pressure one-dimensional compression cell used by Higgins et al. (1997)

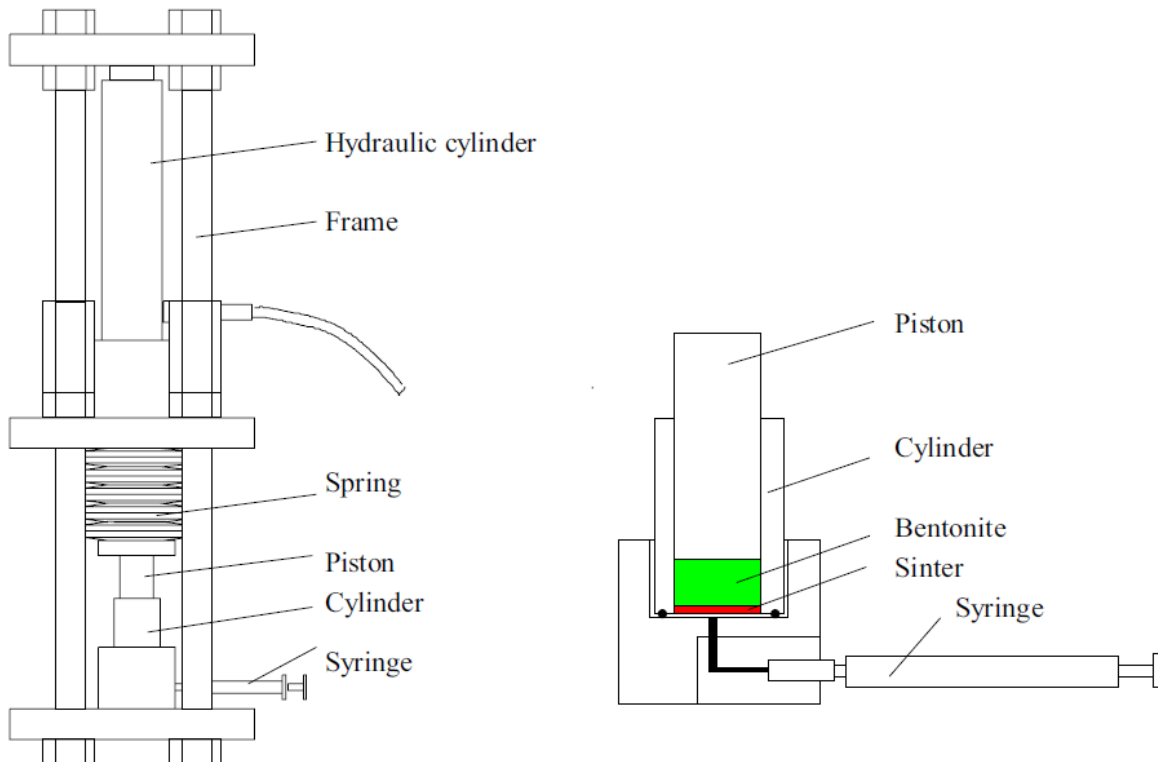


Figure A- 18. Pressing apparatus (left) and compaction cell (right) for squeezing of bentonite porewater. 70-120 MPa, 0.5-3 mL water, 2 cm ϕ /2 cm high sample, 1-2 weeks operation. Muirinen (1999, 2006)



Figure A- 19. Set-up for the extraction of pore water by mechanical squeezing of clay cores. Boom Clay pore water analysis, 30-35 MPa, 40-50 mL water, 700 g sample (8 cm ϕ /10 cm high), 1 week operation. De Craen et al. (2004)

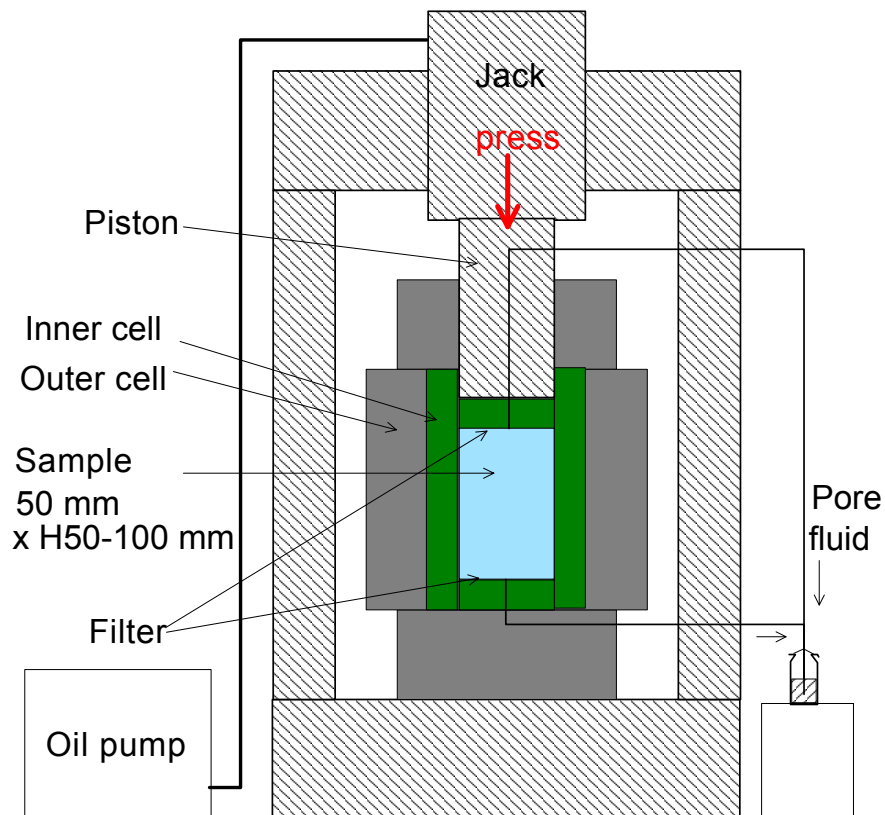


Figure A- 20. CRIEPI'S squeezing device. 30-525 MPa, 0.5-3 mL water, 5 cm ϕ /10 cm high, 1-4 weeks operation (Kiho, 1999)

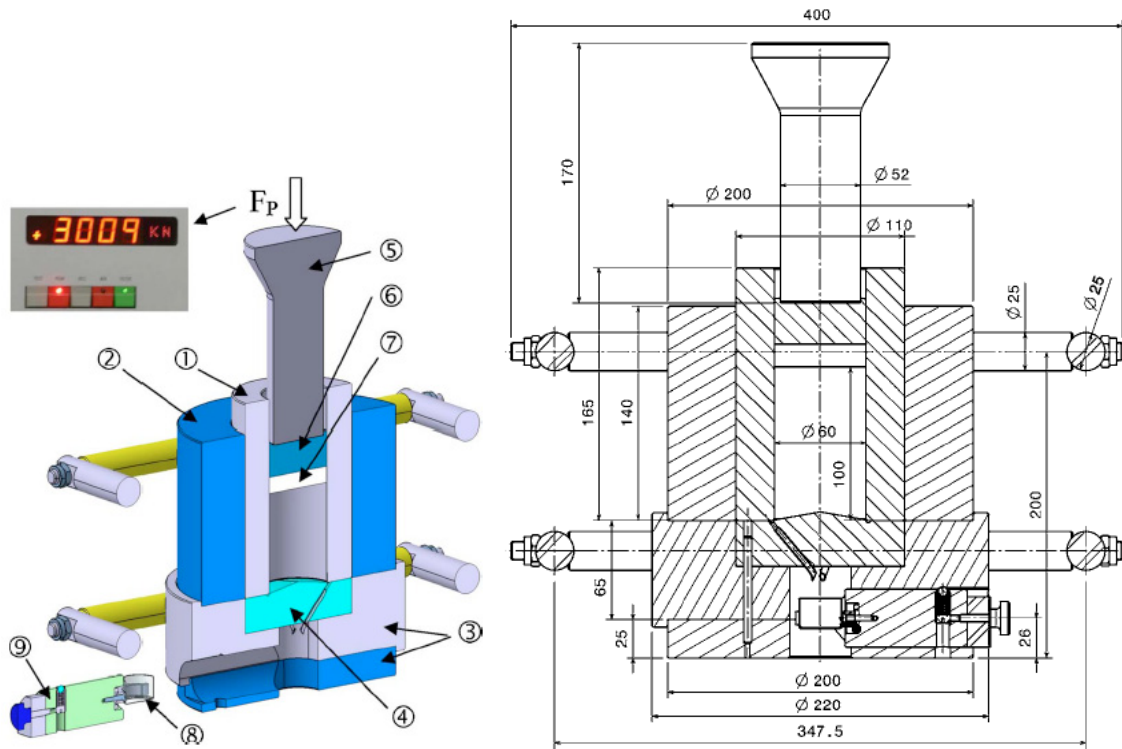
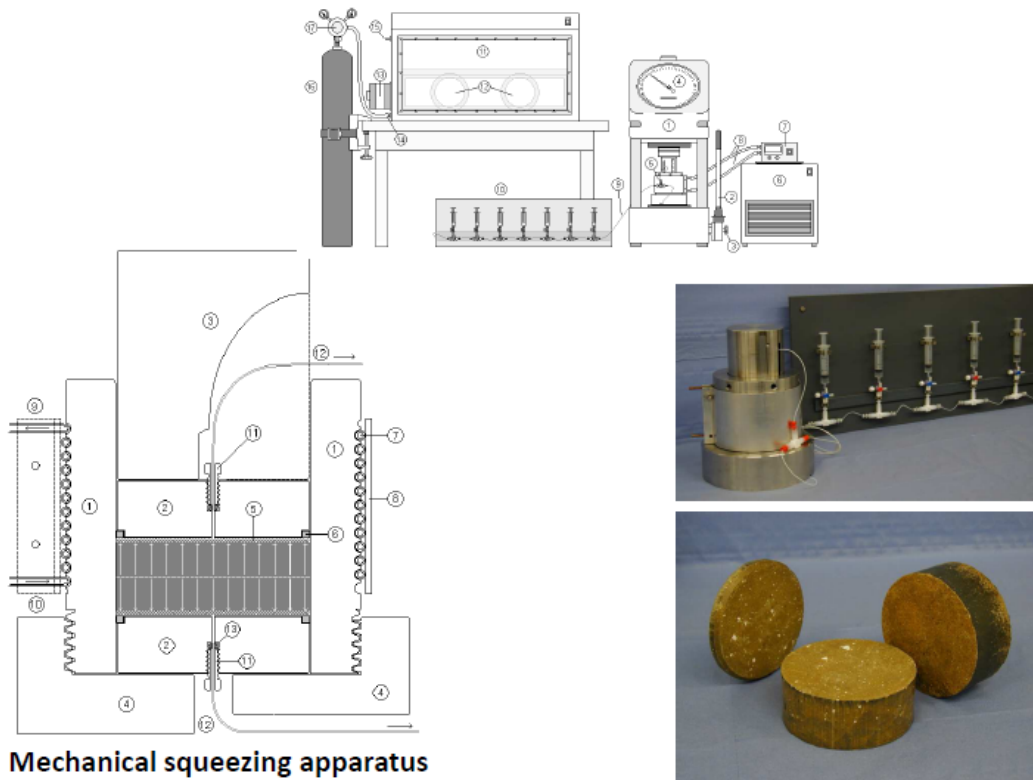


Figure A- 21. Schematic diagram of the high-pressure one-dimensional compression squeezing device for obtaining pressure of up to 600-800 MPa. Cyr and Daidié (2007)



Mechanical squeezer apparatus

Figure A- 22. Mechanical squeezer apparatus. Components: 1) Hydraulic press, 2) Pressure adjusting lever, 3) Pressure release valve, 4) Load gauge, 5) Squeezer, 6) Thermo-regulator, 7) Temperature control unit, 8) In and Out coolant tubings, 9) Main PTFE tubing, 10) Syringe board, 11) Glove box, 12) Hand access windows, 13) Sample and tools entry window, 14) Gas entry port, 15) Gas exhaust, 16) Gas source (cylinder), 17) Gas pressure regulator. Hiscock and Najafi (2011)

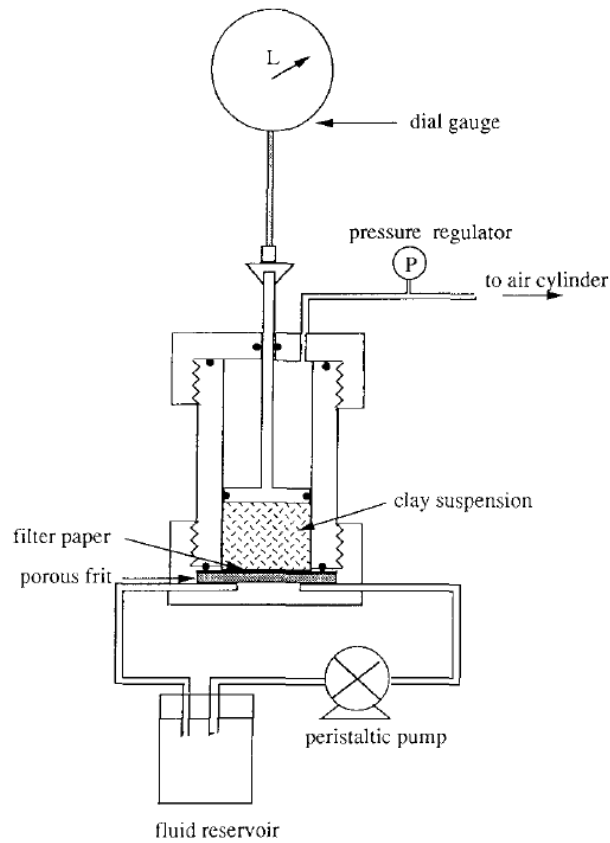


Figure A- 23. Schematic diagram of the oedometer used for the bulk swelling/compaction experiments. Denis et al. (1991)

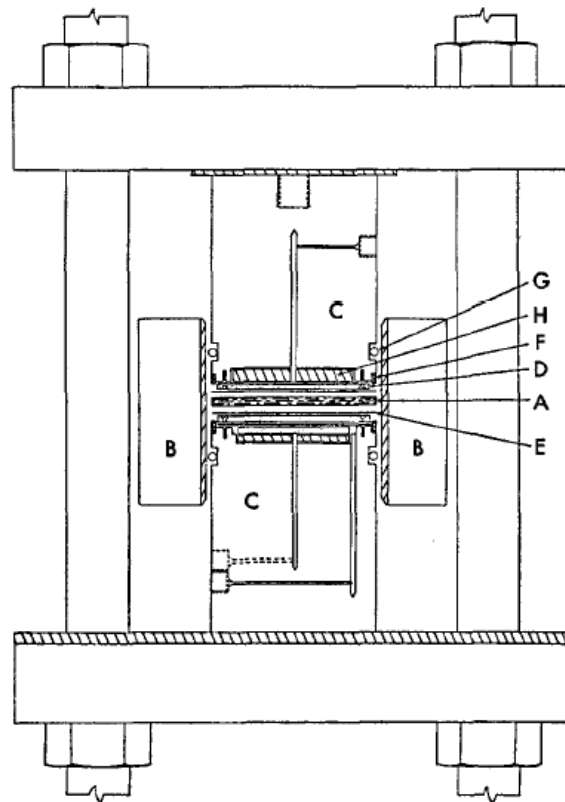


Figure A- 24. Diagrammatic sketch of the filtration flow apparatus: A) Clay sample, B) plastic lined K-monel cylinder, C-K) monel pistons, D-K) monel sintered discs, E) Millipore filters, F) Teflon rings, G-O rings, H) plastic discs. Kharaka and Berry (1973)

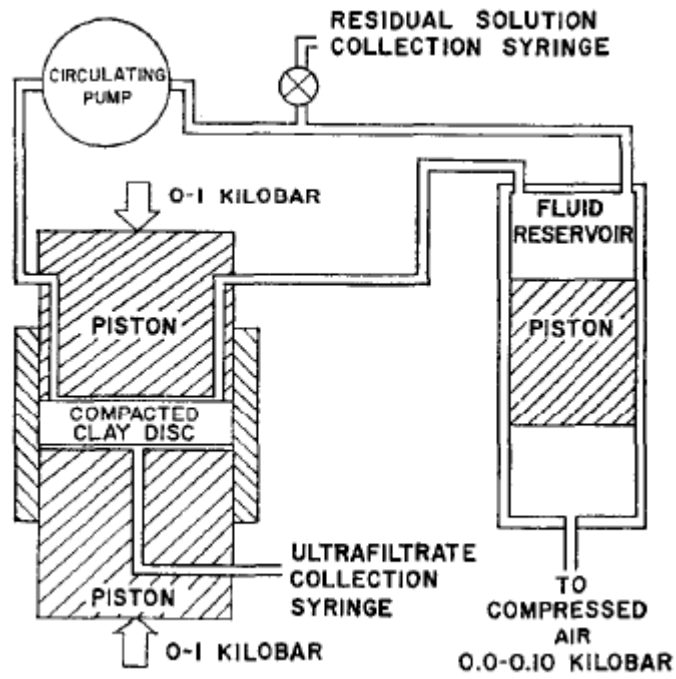


Figure A- 25. Hydraulic press showing experimental set-up.
Olsen (1966), Coplen and Hanshaw (1973)

Annex B. Soluble salts obtained by aqueous leaching

Table B. 1. Soluble salts obtained by aqueous leaching at different solid to liquid ratios for the core samples BHT-1 and BDR-2, in mg/L (interaction time = 48 h)

Core samples	BHT-1					BDR-2			
	S:L ratio	1:1	1:2	1:4	1:8	1:16	1:4	1:8	1:16
g clay: mL water	20.005/20	20.003/40	10.001/40	5.000/40	2.505/40		10.001/40	5.003/40	2.501/40
pH	8.7	9.1	9.3	9.6	9.7		9.2	9.3	9.4
Br (mg/L)	1.7	0.77	0.38	0.2	<0.1		0.2	<0.1	<0.1
Cl⁻ (mg/L)	470	220	110	53	26		65	31	15
NO₃⁻ (mg/L)	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50		<0.50	<0.50	<0.50
SO₄²⁻ (mg/L)	215	110	52	28	14		34	17	8.2
Alkalinity (meq/L)	2.50	2.79	2.73	2.46	1.94		3.49	2.78	2.08
Al (mg/L)	< 0.30	0.84	3.6	9.2	6.3		4	5.9	6.2
Ca (mg/L)	8.0	2.6	1.6	1.5	1.3		1.6	1.4	1.6
Mg (mg/L)	3.6	1.2	1.0	1.6	1.1		1.0	1.1	1.1
Na (mg/L)	450	250	153	95	63		133	85	53
K (mg/L)	20	14	11	9.2	7.3		9.4	8.2	7.7
Sr (mg/L)	0.4	0.13	0.06	0.05	0.04		0.11	0.09	0.08
Fe (mg/L)	< 0.30	0.26	1.1	3.1	2.1		1.2	2	2.1
Mn (mg/L)	0.55	0.05	0.04	0.04	0.04		0.04	0.04	0.03
Ba (mg/L)	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03		< 0.03	< 0.03	< 0.03
B (mg/L)	3.2	2.4	1.8	1.2	0.73		1.4	0.9	0.53
Si (mg/L)	4.1	4.8	10	22	15		9	13	14
E. C. (μS/cm)	2168	1224	806	610	410		709	508	362
I (M)	0.025	0.014	0.009	0.007	0.005		0.008	0.006	0.004

Table B. 2. Soluble salts obtained by aqueous leaching at different solid to liquid ratios for the core samples BWS-A4, BWS-A5, BWS-E4, BWS-A6 and BWS-E6, in mg/L (interaction time = 48 h)

Core samples	BWS-A4			BWS-A5			BWS-E4	BWS-A6	BWS-E6
	S:L ratio	1:2	1:4	1:8	1:2	1:4	1:8	1:4	1:4
g clay: mL water	20/40	10/40	5/40	20/40	10/40	5/40	10/40	10/40	10/40
pH	7.91	8.68 ± 0.17	8.71	8.07 ± 0.14	8.19 ± 0.06	8.63 ± 0.08	8.60 ± 0.01	8.00 ± 0.01	8.85 ± 0.21
Br (mg/L)	< 1	< 1	< 1	< 1	< 1	< 1	< 0.1	0.38 ± 0.01	0.36 ± 0.01
Cl (mg/L)	230	116 ± 14	59	192 ± 9	104 ± 5	48 ± 1	17.00 ± 0.01	137.50 ± 0.71	110.00 ± 1.41
SO₄²⁻ (mg/L)	820	204 ± 40	111	660 ± 67	330 ± 18	172 ± 4	101.50 ± 0.71	314.50 ± 12.02	194.00 ± 5.66
NO₃⁻ (mg/L)	< 1	1	< 1	< 1	< 1	< 1	< 0.1	< 0.1	< 0.1
Alkalinity (meq/L)	3.11	2.89 ± 0.18	2.11	1.98 ± 0.13	1.72 ± 0.05	1.51 ± 0.03	2.83 ± 0.01	1.92 ± 0.01	2.06 ± 0.12
Al (mg/L)	0.2	0.46	0.17	0.24 ± 0.03	0.32 ± 0.07	0.57 ± 0.09	5.10 ± 0.28	0.30 ± 0.00	2.90 ± 0.42
Ca (mg/L)	47	15.3 ± 3.2	4.7	29.5 ± 6.4	13.5 ± 2.1	7.1 ± 0.07	4.50 ± 0.14	15.00 ± 0.00	4.10 ± 0.57
Mg (mg/L)	23	4.2 ± 1.2	1.8	13 ± 2.8	5.2 ± 0.6	2.6 ± 0.1	2.20 ± 0.01	5.25 ± 0.35	1.55 ± 0.21
Na (mg/L)	540	247.5 ± 5.0	140	430.0 ± 14.0	235.0 ± 7.1	125.0 ± 7.1	110.00 ± 0.01	270.00 ± 0.00	202.50 ± 3.54
K (mg/L)	38	17.5 ± 3.1	13	31.5 ± 0.7	21.0 ± 1.4	12.5 ± 0.7	15.50 ± 0.71	17.50 ± 0.71	10.00 ± 0.01
Sr (mg/L)	1.8	0.30 ± 0.08	0.15	1.15 ± 0.21	0.48 ± 0.06	0.22 ± 0.01	0.55 ± 0.00	0.68 ± 0.05	0.15 ± 0.02
Fe (mg/L)	0.19	0.36 ± 0.28	0.08	0.08 ± 0.03	0.14 ± 0.05	0.16 ± 0.03	1.60 ± 0.14	0.06 ± 0.01	0.80 ± 0.12

Table A. 3. Variation of the chemical composition of the pore water with the squeezing pressure in the core samples BHT-1 m. 12.42-12.96 and BDR-2 m. 5.93-6.36, in mmol/L

Core sample	BHT-1 m. 12.42-12.96						BDR-2 m. 5.93-6.36
	75	100	125	150	175	200	125
Sq. Pressure (MPa)							
pH	7.7	7.3	7.04	6.0	6.3	6.0	7.3
Cl (mmol/L)	2.7606·10 ²	2.8169·10 ²	2.7606·10 ²	2.7887·10 ²	2.7887·10 ²	2.8169·10 ²	1.7183·10 ²
SO ₄ ²⁻ (mmol/L)	1.7347·10 ¹	1.8367·10 ¹	1.9388·10 ¹	2.1429·10 ¹	2.1429·10 ¹	2.2449·10 ¹	1.3265·10 ¹
Br ⁻ (mmol/L)	3.7545·10 ⁻¹	3.8171·10 ⁻¹	3.7545·10 ⁻¹	3.7545·10 ⁻¹	3.6294·10 ⁻¹	3.6294·10 ⁻¹	2.4404·10 ⁻¹
NO ₃ ⁻ (mmol/L)	<3.3301·10 ⁻¹	7.1930·10 ⁻¹	<3.3301·10 ⁻¹	<1.3320·10 ⁻¹	3.3301·10 ⁻¹	2.5975	2.2645·10 ⁻¹
Alkalinity (meq/L)	1.82	2.20	4.54	n.d.	2.10	n.d.	1.50
SiO ₂ (mmol/L)	1.1394·10 ⁻¹	1.0681·10 ⁻¹	8.5452·10 ⁻²	n.d.	1.6378·10 ⁻¹	1.5310·10 ⁻¹	6.7649·10 ⁻²
Na (mmol/L)	2.3489·10 ²	2.3924·10 ²	2.3489·10 ²	2.3924·10 ²	2.3924·10 ²	2.3489·10 ²	1.4354·10 ²
K (mmol/L)	1.4067	1.3044	9.2076·10 ⁻¹	7.9287·10 ⁻¹	1.7904	4.3480·10 ⁻¹	5.1153·10 ⁻¹
Ca (mmol/L)	1.6792·10 ¹	1.5220·10 ¹	1.5744·10 ¹	1.6218·10 ¹	1.5719·10 ¹	1.7216·10 ¹	1.1602·10 ¹
Mg (mmol/L)	2.2218·10 ¹	2.0160·10 ¹	2.1477·10 ¹	2.3041·10 ¹	2.2218·10 ¹	2.2629·10 ¹	1.0163·10 ¹
Sr (mmol/L)	5.1358·10 ⁻¹	4.5652·10 ⁻¹	4.9076·10 ⁻¹	5.1358·10 ⁻¹	5.1358·10 ⁻¹	5.2499·10 ⁻¹	5.7065·10 ⁻¹
Fe (mmol/L)	<5.3718·10 ⁻³	≤ 5.3718·10 ⁻³	1.0027·10 ⁻²	<1.2534·10 ⁻²	<6.8043·10 ⁻³	4.4765·10 ⁻²	≤ 5.3718·10 ⁻³
Al (mmol/L)	<1.1119·10 ⁻²	<1.1119·10 ⁻²	<1.1119·10 ⁻²	<2.5944·10 ⁻²	<2.5944·10 ⁻²	≤ 2.9650·10 ⁻²	<1.1119·10 ⁻²
B (mmol/L)	3.5149·10 ⁻¹	3.6074·10 ⁻¹	9.2498·10 ⁻¹	4.7174·10 ⁻¹	6.2899·10 ⁻¹	6.4749·10 ⁻¹	3.0524·10 ⁻¹
Cu (mmol/L)	1.2589·10 ⁻²	<4.7210·10 ⁻³	6.6094·10 ⁻³	<1.1016·10 ⁻²	<5.9799·10 ⁻³	<1.2589·10 ⁻²	<4.7210·10 ⁻³
Mn (mmol/L)	5.8255·10 ⁻²	2.0025·10 ⁻²	1.8205·10 ⁻²	2.5487·10 ⁻²	2.7307·10 ⁻²	2.1846·10 ⁻²	1.1651·10 ⁻²
Mo (mmol/L)	8.1301·10 ⁻³	9.9020·10 ⁻³	7.5047·10 ⁻³	7.9216·10 ⁻³	9.6936·10 ⁻³	1.0423·10 ⁻²	5.7327·10 ⁻³
Ni (mmol/L)	1.2268·10 ⁻²	<5.1116·10 ⁻³	5.2820·10 ⁻³	<1.1927·10 ⁻²	8.8601·10 ⁻³	<1.3631·10 ⁻²	≤ 5.1116·10 ⁻³
Ba (mmol/L)	<2.1846·10 ⁻³	<2.1846·10 ⁻³	2.1846·10 ⁻³	<5.0973·10 ⁻³	<2.7671·10 ⁻³	<5.8255·10 ⁻³	<2.1846·10 ⁻³
Cd (mmol/L)	<2.6688·10 ⁻³	<2.6688·10 ⁻³	<2.6688·10 ⁻³	<6.2271·10 ⁻³	<3.3805·10 ⁻³	1.1565·10 ⁻²	<2.6688·10 ⁻³
Zn (mmol/L)	<4.5879·10 ⁻³	<4.5879·10 ⁻³	1.6822·10 ⁻²	1.8351·10 ⁻²	1.1470·10 ⁻²	<1.2234·10 ⁻²	3.9761·10 ⁻¹

Table A. 4. Variation of the chemical composition of the pore water in the core samples from the boreholes BWS-E6, BWS-A6, BWS-A4, BWS-A5 and BWS-E4, in mmol/L

Core sample	BWS-E6 m. 3.05-3.40	BWS-A6 m. 4.1-4.3	BWS-A4 m. 6.99-9.94			BWS-A5 m. 7.40-7.79			BWS-E4 m. 4.28-4.65
Sq. pressure (MPa)	75	100	87.5	100	125	150	175	200	150
pH	6.8	6.9	7.2	7.3	7.6	7.8	7.8	7.2	8.1
Cl (mmol/L)	$3.0986 \cdot 10^2$	$3.3803 \cdot 10^2$	$2.6761 \cdot 10^2$	$2.6761 \cdot 10^2$	$2.8169 \cdot 10^2$	$2.8169 \cdot 10^2$	$2.8169 \cdot 10^2$	$3.0986 \cdot 10^2$	$7.0423 \cdot 10^1$
SO ₄ ²⁻ (mmol/L)	$1.5306 \cdot 10^1$	$1.7347 \cdot 10^1$	$4.3878 \cdot 10^1$	$4.0816 \cdot 10^1$	$4.6939 \cdot 10^1$	$4.0816 \cdot 10^1$	$4.2857 \cdot 10^1$	$3.8776 \cdot 10^1$	$2.5510 \cdot 10^1$
Br ⁻ (mmol/L)	$4.2551 \cdot 10^{-1}$	$4.3803 \cdot 10^{-1}$	$4.1300 \cdot 10^{-1}$	$4.5054 \cdot 10^{-1}$	$4.2551 \cdot 10^{-1}$	$3.8797 \cdot 10^{-1}$	$4.0048 \cdot 10^{-1}$	$4.5054 \cdot 10^{-1}$	$8.7605 \cdot 10^{-2}$
NO ₃ ⁻ (mmol/L)	$1.0656 \cdot 10^{-1}$	$2.6641 \cdot 10^{-1}$	$1.9980 \cdot 10^{-1}$	$<1.9980 \cdot 10^{-1}$	--	$2.7307 \cdot 10^{-1}$	$3.0637 \cdot 10^{-1}$	$2.7973 \cdot 10^{-1}$	$7.3262 \cdot 10^{-1}$
Alkalinity (meq/L)	$6.6000 \cdot 10^{-1}$	1.61	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.94
Na (mmol/L)	$2.8056 \cdot 10^2$	$2.6969 \cdot 10^2$	$2.6099 \cdot 10^2$	$2.5664 \cdot 10^2$	$2.7621 \cdot 10^2$	$2.6099 \cdot 10^2$	$2.6969 \cdot 10^2$	$2.8491 \cdot 10^2$	$9.1345 \cdot 10^1$
K (mmol/L)	1.5346	1.7648	2.3530	2.1970	1.9950	1.6625	1.3044	1.7904	1.2277
Ca (mmol/L)	$1.6593 \cdot 10^1$	$2.3080 \cdot 10^1$	$2.9942 \cdot 10^1$	$2.5575 \cdot 10^1$	$1.7715 \cdot 10^1$	$1.7965 \cdot 10^1$	$1.7341 \cdot 10^1$	$1.9712 \cdot 10^1$	5.8636
Mg (mmol/L)	$2.4481 \cdot 10^1$	$3.9087 \cdot 10^1$	$3.0858 \cdot 10^1$	$2.9212 \cdot 10^1$	$2.1189 \cdot 10^1$	$1.9749 \cdot 10^1$	$2.0160 \cdot 10^1$	$2.5509 \cdot 10^1$	$1.0492 \cdot 10^1$
Sr (mmol/L)	$5.1358 \cdot 10^{-1}$	$5.2499 \cdot 10^{-1}$	$5.8206 \cdot 10^{-1}$	$6.5054 \cdot 10^{-1}$	$4.4510 \cdot 10^{-1}$	$4.3369 \cdot 10^{-1}$	$4.3369 \cdot 10^{-1}$	$6.3912 \cdot 10^{-1}$	$5.1358 \cdot 10^{-1}$
Ba (mmol/L)	$1.4564 \cdot 10^{-3}$	$3.2040 \cdot 10^{-3}$	$<7.2819 \cdot 10^{-3}$	$<7.2819 \cdot 10^{-3}$	$<2.9128 \cdot 10^{-3}$	$<2.9128 \cdot 10^{-3}$	$<2.9128 \cdot 10^{-3}$	$<2.1846 \cdot 10^{-3}$	$<2.1846 \cdot 10^{-3}$

