



Stable isotopes applied to the study of the concrete/bentonite interaction in the FEBEX *in situ* test

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ABSTRACT

Stable isotope analysis was carried out on a set of samples from the concrete-bentonite interface from the FEBEX real-scale *in situ* experiment. The concrete and bentonite that simulated the engineering barriers system of a deep geological repository have interacted for 13 years in saturated conditions up to dismantling. The monitoring of the experiment during the years of operation has made possible to know not only the baseline status but also the evolution of the system and the mass transfer processes. Thus, the FEBEX experiment has been a unique opportunity to study concrete degradation within a broader multi-proxy approach under real-scale repository conditions.

Analysis of carbon and oxygen isotopes of carbonates in groundwater, concrete and clay have provided evidence of how dissolution and mass transfer processes occur in the Engineered Barrier System (EBS). Spatial distribution of $\delta^{13}\text{C}$ values points to the existence of a dominant process of diffusion of carbon species from bentonite towards the concrete/bentonite interface. Variations in $\delta^{18}\text{O}$ values suggest a non-homogeneous geochemical and hydraulic behavior of the EBS in the vicinity of both, the granite-concrete interface and the concrete-bentonite interface. These differences might be related to different degrees of exposure of each sample to bentonite porewater, groundwater and concrete/bentonite leachates. This seem to be in agreement with the existence of different chemical environments depending on the location of the samples in the experiment.

1. Introduction

Deep geological repository (DGR) is today the best option to keep radioactive waste isolated from the biosphere. It consists of excavating galleries in a rock formation (either granite or clay) at a certain depth and storing the waste in them by the construction of an engineered barrier system (EBS). This includes the encapsulated waste, a layer of expansive clay (bentonite) that covers it and a concrete plug to seal the gallery. This concept of multiple barriers is the key to ensure the containment of wastes for a long time (Chapman, 2006; Alexander and McKinley, 2007; Chapman and Hooper, 2012). Among the investigations carried out to prove the viability of a DGR are those whose objective is to demonstrate that the EBS will maintain its functions during the life of storage, both in terms of its thermo-hydro-mechanical properties as the geochemical and mineralogical ones, so storage will be safe. In relation to this last aspect, the interaction at the system groundwater-concrete-bentonite under repository conditions can favor the occurrence of degradation processes of the concrete plug sealing the galleries, thus compromising its barrier function. So it is necessary to

investigate the origin and extent of the alteration to evaluate the performance of the EBS.

Research has been conducted on the processes that occur by the groundwater-concrete-bentonite interaction on a laboratory scale (e.g. Cuevas et al., 2006; Devol-Brown et al., 2007; García-Calvo et al., 2010, 2013; Dauzères et al., 2010, 2014) and on a real scale in underground laboratories (Tinseau et al., 2006; Gaboreau et al., 2012; Bartier et al., 2013; Jenni et al., 2014; Dauzères et al., 2016; Alonso et al., 2017; Fernández et al., 2017; Lerouge et al., 2017; Mäder et al., 2017). The study of natural analogues (e.g. Maqarin natural analogue in Jordan) has also provided information on the effects of hyperalkaline water on the surrounding material (Milodowski et al., 1989; Khoury et al., 1992; Smellie, 1998) and points to the possibility that the dissolution/precipitation of minerals affects the porosity and the progression of the alkaline plume, which is important to ensure the repository performance. Despite the chemical differences between the types of groundwater (granite or clay), concrete (high or low pH) and clays investigated (bentonite or clayey rock), one of the processes commonly observed in laboratory investigations, real-scale *in situ* experiments and

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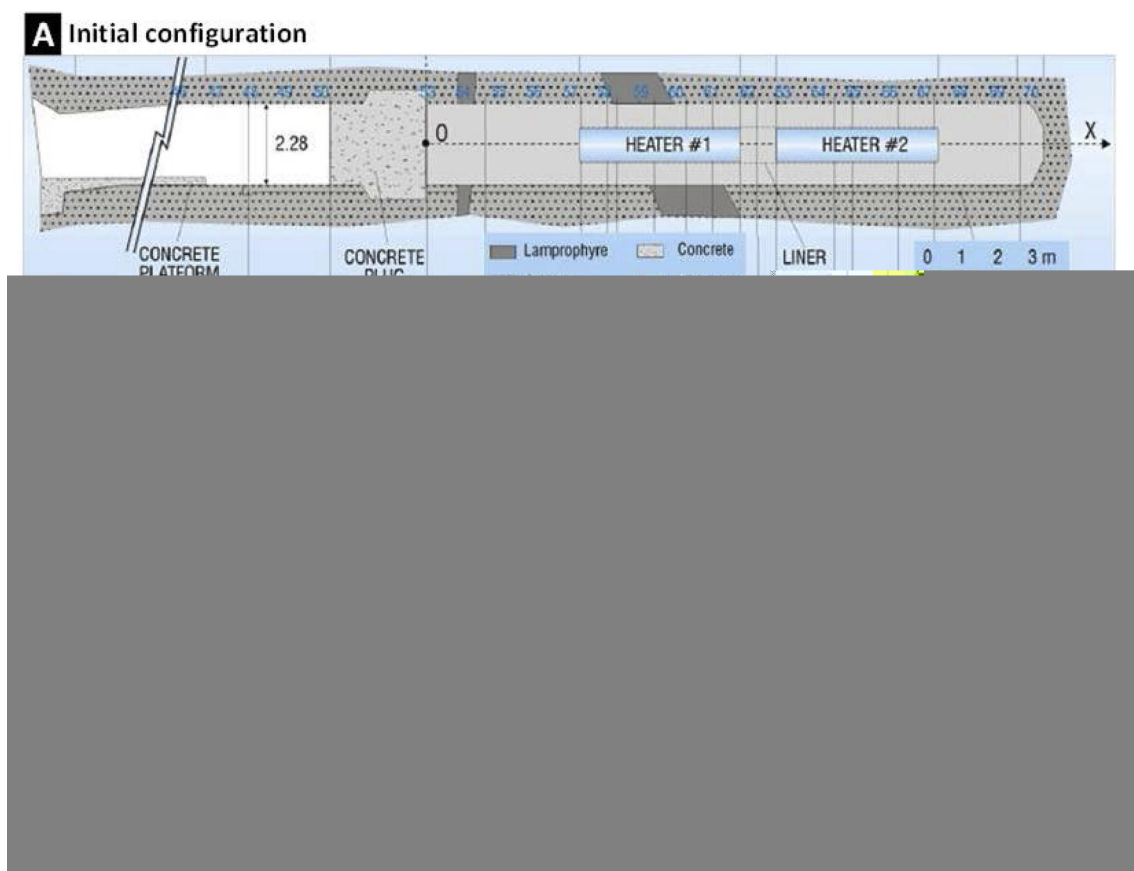


Fig. 1. A. Initial configuration of the FEBEX experiment. It was in operation for 5 years (1997–2002) (Huertas et al., 2006). B. Configuration of the FEBEX experiment after the first dismantling (Huertas et al., 2006). It was in operation until 2015, when the experiment was completely dismantled. C. Location of boreholes for groundwater sampling around the FEBEX gallery (details in Garralón et al., 2017). D. Simplified picture showing sampling position (rectangles) and water fluxes under consideration.

natural analogues is the dissolution/precipitation of carbonates due to the interaction between materials until the system reaches equilibrium. Then the carbonation of the concrete and the subsequent precipitation of secondary calcite takes place (e.g. Gaboreau et al., 2012; Dauzères et al., 2014; Fernández et al., 2017; Lerouge et al., 2017).

The processes of dissolution-precipitation of calcite leave their imprint in the isotopical values of the oxygen and carbon, which will help to identify its origin. In natural scenarios, the combination of $\delta^2\text{H}$, $\delta^{18}\text{O}$ and d -excess has been extensively used to trace water sources, mixing and geochemical processes along a flow path (Yurtsever and Araguás, 1993; Kendall and McDonnell, 1998; Schulte et al., 2011; Halder et al., 2015). On the other hand, carbon-13 is an excellent tracer of carbonate evolution in groundwater because of the large variations in the various carbon reservoirs. Therefore, analysis of carbon and oxygen isotopes of carbonates in groundwater, concrete and clay can provide evidence of how dissolution and mass transfer occur in the system. To date, several studies have been carried out on the potential for the use of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the field of concrete degradation, generally focusing on the characterization of historic mortar for conservation and restoration purposes (Rafai et al., 1992; Letolle et al., 1992; Macleod et al., 1991; Iden and Hagelia, 2003). The isotopic changes of the initial $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in the mortar matrix are usually related to the alteration of the primary source of CO_2 and H_2O over time, in particular by re-crystallization of calcite with porewater, evaporated or re-condensed water, and CO_2 from various sources of atmospheric and biogenic origin.

Variation in stable isotopic composition have provided information relative to the origin of the CO_2 and water during calcite formation and the degradation of the mortar. However, there are not many works

based on stable isotopes that have been devoted to the analysis of the mass transfer processes that cause the precipitation of carbonates in the interfaces between different materials in the EBS (e.g. Gaboreau et al., 2012; Fernández et al., 2017). In that context, the FEBEX real-scale *in situ* test (ENRESA, 1995) excavated in the Aare granite in the Swiss Alps (www.grimsel.com) has provided a unique opportunity to determine the isotopic signature of groundwater, concrete and bentonite in a broader multi-proxy approach that attempts to obtain further insight into the concrete/bentonite interaction under real-scale repository conditions.

Results on mineralogical analysis of the concrete-bentonite interface of the FEBEX experiment were presented in Alonso et al. (2017), Fernández et al. (2017) and Turrero and Cloet (2017). In those works, aqueous extracts analyses, images and analysis by scanning (transmission) electron microscopy/energy dispersive X-ray spectroscopy, X-ray diffraction, thermogravimetric analysis and infrared measurements were compiled showing mass transfer of carbonate species between materials and the precipitation of calcite in the interface. The set of results obtained together with some preliminary results of isotopes collected in two concrete-bentonite samples included in the work by Fernández et al. (2017) led to launch the hypothesis of the decalcification of the concrete, dissolution of primary calcite, diffusion of carbonate species and re-precipitation of secondary calcite at the interface both on the concrete side and on the bentonite side.

The purpose of the investigation presented here was to track the evolution of the carbonate system after the groundwater-concrete-bentonite interaction in the FEBEX experiment, in terms of origin, movement and distribution of carbon species in the EBS. The work has as starting point the baseline conditions of the experiment, and

attempts to explain its evolution based on the analysis of stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$ and $\delta^{13}\text{C}$) of the groundwater, concrete and bentonite samples taken at different points of the FEBEX experiment, some close to the granite, others taken at the concrete-bentonite interface, both on the concrete side and on the bentonite one, and samples of both materials far from the interface.

2. Description of the FEBEX in situ experiment

The FEBEX *in situ* was a full-scale experiment to check the viability of the Spanish concept for the DGR in granite formations, that consists on waste canisters placed horizontally in drifts, surrounded by a clay barrier constructed from highly-compacted bentonite blocks (ENRESA, 1995). It comprised two phases, the first one (FEBEX I) for construction and the second one (FEBEX II) to study thermo-hydro-mechanical and thermo-hydro-geochemical processes that served to validate numerical codes.

The experiment was placed in 1996 in the Grimsel underground laboratory (Swiss Alps), which is excavated in granite (www.grimsel.com). The thermal effect of the wastes was simulated by means of heaters adjusted to a temperature of 100 °C and the hydration occurred naturally with the groundwater of the granite, a quite diluted Ca-Na-HCO₃ type water (see details in Garralón et al., 2017). The configuration of the test is depicted in Fig. 1A. The gallery excavated in granite had dimensions of 70 m long and 2.3 m in diameter. Two heaters with dimensions and weights analogous to those of the real canisters were installed inside a liner concentric to the gallery and separated from each other 1 m. The gap between the heaters and the granite was filled with blocks of compacted bentonite. The set was instrumented and monitored throughout the duration of the experiment.

The clay barrier was made of FEBEX bentonite, which was extracted from the Cortijo de Archidona deposit (Almería, Spain). The physico-chemical properties of the FEBEX bentonite, as well as its most relevant thermo-hydro-mechanical and geochemical characteristics are summarized in Huertas et al. (2006). The heating stage began on February 1997. After five years of uninterrupted heating at constant temperature (February 2002) the heater closer to the gallery entrance (heater #1) was switched off (Bárcena et al., 2003; Huertas et al., 2006). In the following months this heater and all the bentonite and instruments preceding and surrounding it were extracted. The remaining part of the experiment (heater #2) was sealed with a shotcrete plug made with Portland cement CEM II A-L 32,5 R (Fig. 1B). Details of the operations for constructing the plug are given in Huertas et al. (2006). It was constructed in two stages: a first section (S1) with a thickness of 1 m and a second one of two meters (S2), giving a total length of 3 m.

Fifteen boreholes were drilled in 1996 in the test zone from the inner part of the FEBEX drift radial to the gallery (Huertas et al., 2006). The length of the boreholes varied between 7 and 22 m, with a total of 233 m drilled. The boreholes' position is shown in Fig. 1C. In order to avoid mixing of the different types of waters, all the boreholes were equipped with multipacker systems. Water pressures were measured continuously and could be monitored by remote control (AITEMIN, 2004). Two additional boreholes for hydro-geochemical investigation (named FU-1, FU-2) were drilled parallel to the gallery at the end of 2005 in order to investigate the geochemical processes related to the

solutes' migration in crystalline rocks (Pérez-Estaún et al., 2006; Buil et al., 2010). Granite groundwater was sampled from radial and parallel boreholes in 16 sampling campaigns conducted between 1996 and 2016, the last one when the experiment had been completely dismantled. Chemistry and stable isotopes were characterized in samples from the boreholes, both radial and parallel, to trace the geochemical processes involved in the evolution of the experiment (Garralón et al., 2017).

The experiment was fully dismantled in 2015 (García-Siñeriz et al., 2016; Villar et al., 2016). The detailed sampling plan to investigate the state of the EBS can be found in Bárcena and García-Siñeriz (2015a) and Bárcena and García-Siñeriz (2015b). In <http://www.grimsel.com/gts-phase-vi/febexdp/febex-dp-introduction> an animation about dismantling and details about sampling can be found. At the time of the dismantling of heater #2 the concrete plug had been interacting with the bentonite and the granite for 13 years and in the area of the concrete-bentonite interface the bentonite was fully saturated (Villar et al., 2016) and there was a temperature of about 30 °C (Mäder et al., 2016). Concrete-bentonite samples were extracted to analyze the effects of the alkaline plume on the properties of the bentonite and the influence of the bentonite pore water on the properties of the concrete (Fig. 1D). The details of sampling are given in the next section.

3. Materials and methods

3.1. Groundwater

The ageing of the EBS in the FEBEX *in situ* test was addressed in the context of hydrogeochemical processes of the EBS-granite system. For that purpose, a total of 16 samplings campaigns were done in order to track the variations on the chemical composition of the groundwater in the surrounding of the FEBEX experiment. Those changes were supposed to be originated mainly by the interaction of the bentonite barrier in contact with the granite host rock during the years 1996–2016 (Garralón et al., 2017).

Representativeness of water samples of the on-site conditions was an issue of concern when planning groundwater sampling. Groundwater samples were collected from packed-off zones in the boreholes to a flow cell isolated from the atmosphere. Polyamide tubing (an inert material impervious to O₂ diffusion) was used to transport the water from the boreholes during the sampling. The flow rate ranged from 0.01 ml/min in the less permeable sections to 500 ml/min in isolated fractures with higher transmissivity. Preservation was undertaken according to the constituents under analysis. Stable isotopes were collected in fully filled PP-15 ml bottles to prevent evaporation of water. The samples were transported to the laboratory in a thermostatic box at 4 °C.

The water sampled in the radial boreholes had a neutral or slightly alkaline pH and an average electrical conductivity of $101 \pm 31 \mu\text{S/cm}$. The chemical composition of Grimsel's water is the result of the interaction with granite and the minerals that fill the fractures. Dissolution of carbonates and silicate minerals by groundwater recharge has led to the formation of Ca-Na-HCO₃ type water (Table 1).

The initial chemical composition of the groundwater sampled in the packed-off sections of the two parallel boreholes was also Ca-Na-HCO₃.

Table 1

Chemical composition of bentonite porewater, Grimsel granite water (mean of the chemical composition of radial boreholes) and water in contact with the concrete plug close to the dummy canister.

	pH	CE					meq/l						% SMOW	
		$\mu\text{S/cm}$	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	Na	K	Ca^{2+}	Mg	$\delta^{18}\text{O}$	$\delta^2\text{H}$		
Granite groundwater	8.1	104	0.1	0.2	0.7	–	0.5	0.0	0.6	0.0	–12.5	–90.1		
Bentonite porewater	7.4	13230	112.7	26.3	16.1	–	91.3	0.4	25.4	32.2	–5.3	–50.0		
Water spill	10.2	10850	23.0	18.0	4.9	55.2	114.5	13.5	3.1	0.3	–8.2	–69.1		

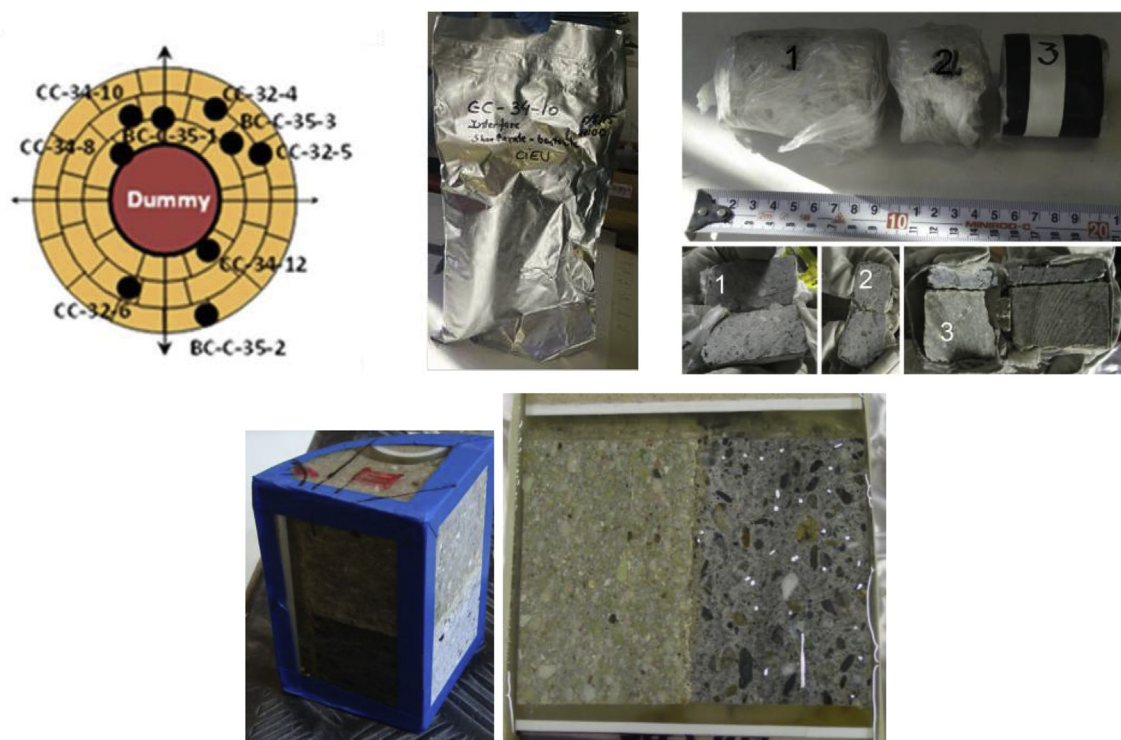


Fig. 2. (Up-Left) Frontal view of the bentonite in the FEBEX experiment with the location of concrete-bentonite samples analysed for this work. (Up-Right) Core sample C-C-34-10 in the Al-sheet and after opening for analysis. (Down) Image of the concrete-bentonite interface of the overcoring C-C-32-5 with 5 cm of each material.

The chemical composition evolved over time to a Na-Cl type water. In fact, five different types of water (Ca-Na-HCO₃, Ca-Na-SO₄, Na-Ca-SO₄, NH₄-SO₄ and Na-Cl) were found as a function of two main factors: the distance to the bentonite barrier and the saline composition of the bentonite porewater (Buil et al., 2010; Garralón et al., 2017). It has been interpreted as there is a mass transfer from the bentonite into the granite.

During the dismantling operations of the second heater (May'15), a water spill occurred close to sample C-C-34-12 (Fig. 2). It was collected in a polypropylene bottle of 30 ml and analysed. Its analysis revealed that it was a Na-CO₃-type groundwater with high chloride, sulfate and potassium contents (Table 1). Electrical conductivity, pH and chemical composition indicate that water collected from the spill is a mixture of granite groundwater, concrete and bentonite porewater.

Since the main chemical gradients in the system are due to the interaction of granite groundwater and/or bentonite porewater with other components of the experiment the isotopic measurements were focused in the study of the alteration processes occurring in the concrete-bentonite interface due to the interaction with the different types of water fluxes in the EBS system.

3.2. Concrete-bentonite cores

The bentonite used in the experiment was the FEBEX bentonite, that has a content of dioctahedral smectite of the montmorillonite type of $92 \pm 3\%$ and contains variable quantities of quartz ($2 \pm 1\%$), plagioclase, cristobalite ($2 \pm 1\%$), potassium feldspar traces, calcite (traces) and trydimite (traces). The cation exchange capacity is 102 meq/100 g, and the exchangeable cations are Ca (35 ± 3 meq/100 g), Mg (31 ± 3 meq/100 g), Na (27.1 ± 0.2 meq/100 g) and K (2.6 ± 0.4 meq/100 g). FEBEX bentonite porewater is Na-Cl-type water with high magnesium and calcium contents. Its average EC value is 13230 μ S/cm and its pH is neutral (~ 7.4) (Table 1) (Fernández et al., 2004).

The composition of the concrete plug consisted of 430 kg/m³ of CEM II A-L 32.5 R, 30 kg/m³ of nanosilica MEYCO MS 660; 50 kg/m³ of steel fibres Dramix ZP 306; 800 g/m³ of polypropylene fibers; 1.5% of superplasticizer GLENIUM T803; water/cement ratio = 0.40; 1700 kg/m³ of aggregate 0–8 mm; 1% of curing compound MEYCO TCC 735 and 6% accelerant MEYCO SA 160 E. According to the manufacturer this accelerator had a high Al content, thus promoting ettringite formation to obtain the initial fast hardening required (Alonso et al., 2017).

Sampling and analysis of concrete-bentonite cores were planned to obtain data at the interface scale (mm) and at the scale of centimetres. Nine samples comprising the concrete-bentonite interface were analysed in this study (Fig. 2, left). Five of those samples (C-C-34-8, 10 and 12, and BC-C-35-1 and 2, example in Fig. 2, up-right) were obtained by dry-drilling with a diamond coring Hilti® machine. Around 10 cm of concrete and 5–8 cm of bentonite were obtained in each core sample. When the demolition of the plug was almost done, pieces of concrete were easily detachable, and then hand-picked concrete samples were collected as well as bentonite contacting them, which was cut with a knife and extracted. One of these concrete-bentonite bulk samples, named as BC-S-35-3, has been used for this study. All the samples were immediately sealed under vacuum in Al-sheets for further investigations on the interface. Samples named C-C-32-4, 5 and 6 were obtained by the University of Bern using the stabilized overcoring technique (Mäder et al., 2016). The samples were packed under vacuum at the FEBEX location, kept in cold storage and moulded entirely in epoxy resin at the University of Bern, as described in Mäder et al. (2016). In Fig. 2 (down) a photo of the concrete-bentonite interface of the overcored sample C-C-32-5 is presented.

As alteration processes occurs mainly in the vicinity of the interface, a detailed sampling was required in the first centimetre at both sides of the interface. In the first centimetre, concrete and bentonite were sampled, when possible, at each 2 millimetres. In order to establish the baseline isotopic signature of concrete in the FEBEX *in situ* test, concrete was sampled at 88, 50 and 5 cm from the interface in cores drilled at

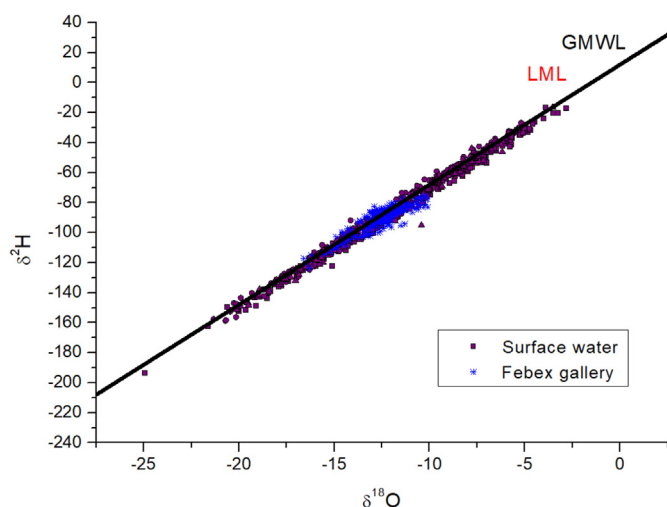


Fig. 3. Variation of the values of $\delta^2\text{H}$ vs $\delta^{18}\text{O}$ of the meteoric waters sampled at the surroundings of the Grimsel Test Site. Also, are plotted the values of the waters from the boreholes of the FEBEX gallery (radial and parallel). The Global Meteoric Water Line (GMWL, $\delta^2\text{H} = 8\delta^{18}\text{O} + 12$), is almost exactly the same as that calculated as Local Meteoric Line (LML, $\delta^2\text{H} = 8.2\delta^{18}\text{O} + 12.5$).

different positions in the experiment. Several $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements of raw FEBEX bentonite together with isotopic values obtained for bentonite samples collected at different distances from the interface and different positions in the experiment were used to define the baseline conditions for the bentonite barrier.

For high precision sampling, a Dremel® Multi-tool was used. For the drilling of the bentonite and the concrete specimens, Tungsten carbide drill bits were chosen. Sampling was performed by slow drilling to minimize chipping. Drill bits were placed perpendicular to the surface of the core. Powder obtained after drilling the first 3 mm into the sample was discarded in order to avoid surface contamination. A minimum of 0.25 g of powder was collected for isotopic analysis. Duplicates were made of all the samples and in some cases tripled.

3.3. Analytical techniques

3.3.1. Measurement of $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in water samples

Hydrogen and oxygen stable isotope ratios ($^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$) were determined by means of Cavity Ring-down Spectroscopy (CRDS). Stable isotopes of oxygen (^{18}O) and deuterium (^2H) were analysed with a Picarro L2120 water isotope analyzer (Santa Clara, CA, USA) with a precision of $< 0.1\text{‰}$ for ^{18}O and $< 0.3\text{‰}$ for ^2H .

Determination of the $^{13}\text{C}/^{12}\text{C}$ isotope ratio in water samples was performed with a Picarro G1101-i, which allows real-time quantification of $^{12}\text{CO}_2$, $^{13}\text{CO}_2$ and $\delta^{13}\text{C}$ with a precision better than 0.3‰ for ^{13}C and a carbon dioxide (^{12}C) sensitivity of 50 parts-per-billion (ppbv).

Each sample was injected six times into the vaporizer. Memory effects from previous samples were avoided by rejecting the first three analyses. Values for the final three injections were averaged with in-run precision of less than ± 0.1 for $\delta^{18}\text{O}$ and ± 0.5 for δD (1 σ). Calibration of results to V-SMOW, the IAEA reference standard, was achieved by analyzing V-SMOW2 (Vienna Standard Mean Ocean Water 2), GISP (Greenland Ice Sheet Precipitation), and SLAP (Standard Light Antarctic Precipitation) standards before and after each set of eight samples. All results are reported in parts per thousand relative to V-SMOW. The certified values are referred to its isotopic relations $^{18}\text{O}/^{16}\text{O}$ as well as to $^2\text{H}/^1\text{H}$, expressed by $\delta^2\text{H} \text{‰}$ and $\delta^{18}\text{O} \text{‰}$, and allow a linear fit in a wide range of δ values.

The isotopic analysis of the FEBEX bentonite porewater and concrete plug porewater were determined using the methodology described in Garraón et al. (2017). Additionally, in order to confirm the validity

of that method, an extraction at 105°C with a nitrogen flow was done, with retention of the vapor phase in a cold trap. In order to avoid undesired fractionation processes, the extraction has to be close to 100%. The obtained results of both methods were similar.

3.3.2. Measurement of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in concrete and bentonite samples

Carbon and oxygen isotopes ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) in the bentonite and the concrete were measured by Isotope-Ratio Mass Spectrometry (IRMS). Measurements were performed on a GB/GC-Thermo Delta V Advantage equipment coupled to a Gas Bench II (Thermo) system. Samples were weighed into exetainers vials. H_3PO_4 (85% Merck reagent) was added to samples in the exetainers, that were previously vacuum dried. Reaction at $72 \pm 1^\circ\text{C}$ for 18 h was followed by analysis by continuous flow IRMS. Analytical precision (2 sigma) is $\pm 0.1\text{‰}$. Data for C and O were normalized using international standards (V-PDB) NBS-18, IAEA CO1, IAEA CO8 and IAEA CO9, in addition to an in-house laboratory standard (marble). Fraction $> 0.05 \text{ mm}$ in concrete samples was discarded for the analyses of stable isotopes, in order to obtain representative measurements of the cement matrix.

4. Results and discussion

4.1. Isotopic data of the groundwater hydrating the system

The stable isotope characterization of meteoric, surface and groundwater in the surroundings of the FEBEX gallery facilitated the understanding of the processes involved in the geochemical evolution of the EBS system.

Global Meteoric Water Line (GMWL) was obtained according to the equation defined by Craig (1961), where $\delta^2\text{H} = 8\delta^{18}\text{O} + 12$. The Local Meteoric Line (LML) was calculated on the basis of the isotopic data provided by the Grimsel weather station (IAEA/WMO, 2015). Isotopic values measured in meteoric waters ranged from -150 to -30‰ for $\delta^2\text{H}$ values, and from -20 to -5‰ for $\delta^{18}\text{O}$ values.

In Fig. 3, GMWL and LML are plotted together with isotopic data measured in surface water samples and groundwater sampled in radial and parallel boreholes in the FEBEX gallery. Almost-coincident slopes were obtained for the LML and GMWL, for that reason, LML cannot be distinguished from GMWL. As can be seen in Fig. 3, most of the water samples (surface waters and groundwaters) from the FEBEX gallery fall within the LML.

Assuming that the origin of the recharge of the waters in the FEBEX gallery is the meteoric water in the surroundings of Grimsel Test Site, it was expected that groundwater isotopic values fell within LML. However, the comparison between the isotopic signatures of the meteoric waters and groundwater samples from the FEBEX gallery show a significant shift towards more positive values, especially in the case of the parallel boreholes (FU-1, FU-2). These shifts could be related to either evaporation or mixing processes with water of different origins (e.g. bentonite or concrete porewater). To verify the influence that the water of the bentonite could have on the modification of the isotopic signal of the granite water in the vicinity of the EBS, the isotopic signal of three types of water was considered (data in Table 2): the interstitial (structural) water of the bentonite (Caballero and Jiménez de Cisneros, 2011), the bentonite porewater (“accessible” water) (Garraón et al., 2017) and the water obtained during the sampling of the concrete-bentonite interface, named spill water (this work). The results are represented in Fig. 4. The linear relationship of this data set seems to point to the influence of bentonite porewater on the water from the granite formation more than an evaporation process. A further discussion about this influence can be found on Garraón et al. (2017).

In fact, the isotopic and chemical composition of the water spill sampled at the contact between the concrete plug and the bentonite barrier suggests that this spill is mostly composed by a mixture of granitic water and bentonite porewater (Fig. 5). A different level of mixing can be found if is also considered the sample CC-32-5, that also

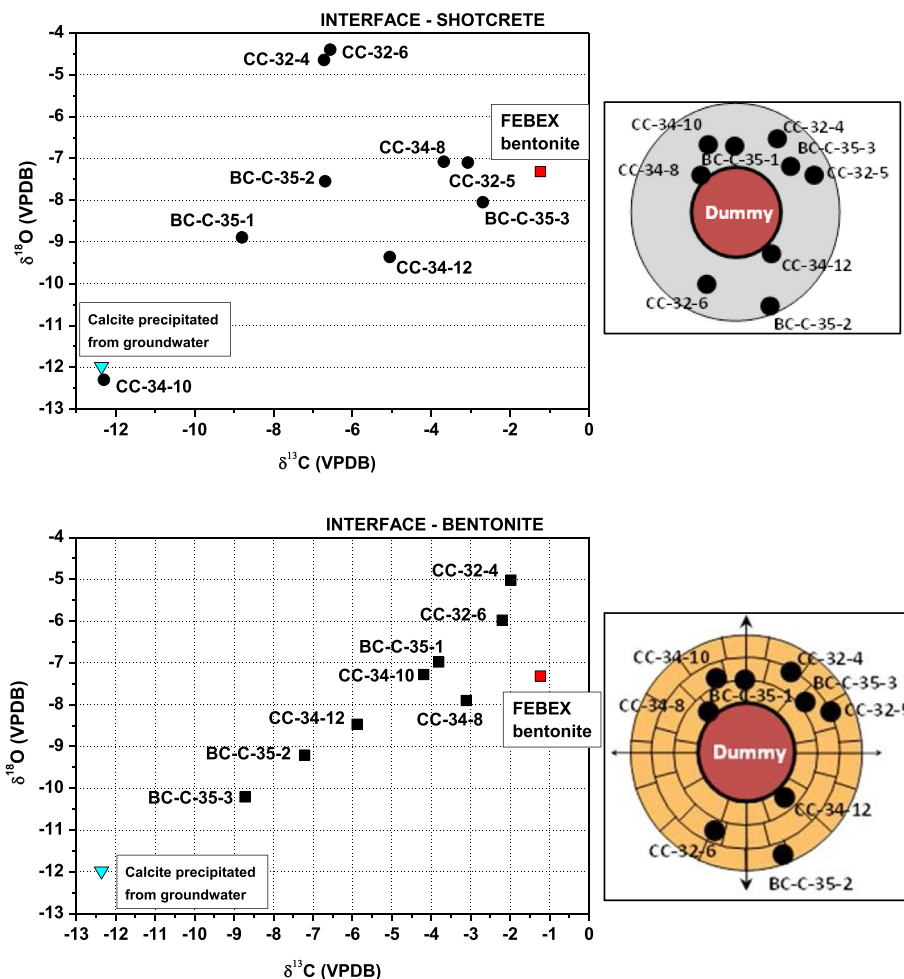


Figure 7. $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$ values measured in the contact between the concrete plug and the bentonite barrier: (a) concrete side; (b) bentonite barrier. The theoretical value calculated for a calcite formed by precipitation of the inorganic carbon present in the groundwater is included (see explanation in the text).

$$1000 \ln \alpha_{\text{calcite-water}} = 17.4 (100/T) - 28.6 \quad (2)$$

(T in Kelvin) (Coplen, 2007; Kim & O'Neil, 1997).

For the calculation of the $1000 \ln \alpha_{\text{calcite-water}}$ value ($\approx \Delta^{18}\text{O}_{\text{calcite-water}} = \delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}$), isotopic values in the VSMOW-scale were used. The conversion of the $\delta^{18}\text{O}_{\text{calcite}}$ values from VPDB to VSMOW standard is given by equation (3):

$$\delta^{18}\text{O}(\text{VSMOW}) = 1.03091(\text{VPDB}) + 30.91 \quad (3)$$

(Hoefs, 2009).

For the estimation of the $\delta^{13}\text{C}$ of the solution in which calcite was formed, a $\alpha_{\text{calcite-water}}$ of 1.00185 was used (Dietzel et al., 2016). In all cases, an average temperature of 20 °C was used for the calculations of the isotopic fractionation.

In the case of calcite precipitated from CO_2 , $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were calculated regarding the isotopic composition of the atmospheric CO_2 in the FEBEX gallery (Table 3). According to this calculations, if calcite

Table 3

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values measured in local meteoric water, Grimsel groundwater and the atmospheric CO_2 in the FEBEX gallery.

	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
Local meteoric water	n.d. ^a	$-13.6 \pm 3\text{‰}_{\text{VSMOW}}$
Granite groundwater	$-14.2\text{‰}_{\text{V-PDB}}$	$-12.1 \pm 0.8\text{‰}_{\text{VSMOW}}$
Atmospheric CO_2 in FEBEX gallery	$-16.6\text{‰}_{\text{V-PDB}}$	$+10 \pm 2\text{‰}_{\text{V-PDB}}$ ^b

^a Could not be determined due to low HCO_3^- concentration.

^b Accepted range throughout the past 2000 years (Dietzel et al., 2016).

matrix had been formed directly by the absorption of CO_2 from the atmosphere in highly alkaline aqueous environment ($\text{pH} > 11$), $\delta^{13}\text{C}_{\text{matrix}}$ of -25‰ and $\delta^{18}\text{O}_{\text{matrix}}$ of -20‰ VPDB are obtained (Kosednar-Legenstein et al., 2008).

A positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values was observed in most of the concrete and bentonite samples. This covariation could a priori be interpreted as an indicator of occurrence of alteration processes in the interface due to the interaction between the concrete plug, the bentonite barrier and the Grimsel groundwater. A closer look at the interface shows that in bentonite samples, $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$ values exhibit a strong positive correlation in most cases. This fact could be related to an increasing influence of groundwater in the neoformation of the secondary calcite found in the bentonite side of the interface.

In the case of the samples collected in the concrete plug, no correlation is observed. However, it should be pointed out that $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values measured in sample C-C-34-10 are close to the ones expected for a calcite formed by the precipitation of dissolved inorganic carbon in Grimsel groundwater.

Fig. 8 and Fig. 9 show the distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values as a function of the distance from the concrete-bentonite interface. The concrete-bentonite interaction is more intense at the interface. In most measured samples, a significant shift towards more negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values is repeatedly observed at the interface. This shift might be caused by the infiltration of granite groundwater through the interface discontinuity and the formation of calcite from the precipitation of the dissolved carbonate. This neo-formed calcite would be $\delta^{13}\text{C}$ -depleted and lead to a significant decrease of $\delta^{13}\text{C}$ at the interface. The

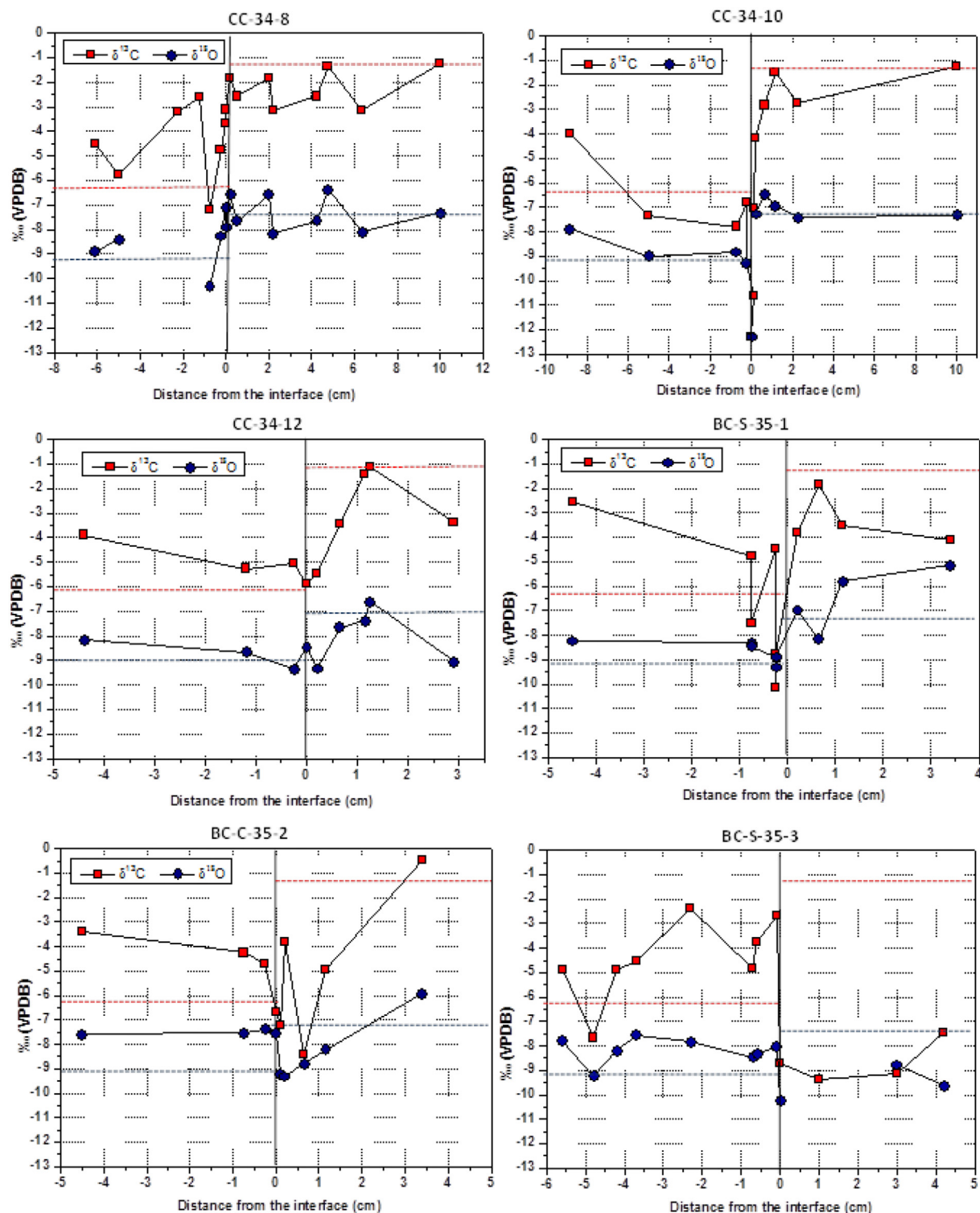


Fig. 8. Evolution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in the concrete-bentonite interface in samples: CC-34-8, CC-34-10, CC-34-12, BC-S-35-1, BC-C-35-2 and BC-S-35-3.

precipitation of secondary calcite in concrete due to carbonate diffusion from bentonite should result in a shift into more positive values and could explain values measured in the concrete side of the interface.

At the same time, $\delta^{13}\text{C}$ values tend to shift towards more positive values in the first centimeters of the concrete plug from the contact with the bentonite barrier. These changes in the isotopic signature of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values near the interface could be related to the precipitation of secondary calcite of two different origins: dissolved carbonate in groundwater and carbonate from bentonite porewater. Shifts towards

more positive values appear to be associated with carbonate diffusion from the bentonite side, whereas shifts towards more negative values seem to be related to an increasing exposure to groundwater. Isotopic signatures of neo-formed calcite in concrete and bentonite sampled at both sides of the interface point to different degrees of interaction between the concrete plug and the bentonite barrier depending on their position in the gallery.

The analysis of $\delta^{18}\text{O}$ values was more complex since the $^{18}\text{O}/^{16}\text{O}$ ratio may be controlled not only by primary calcite dissolution but by

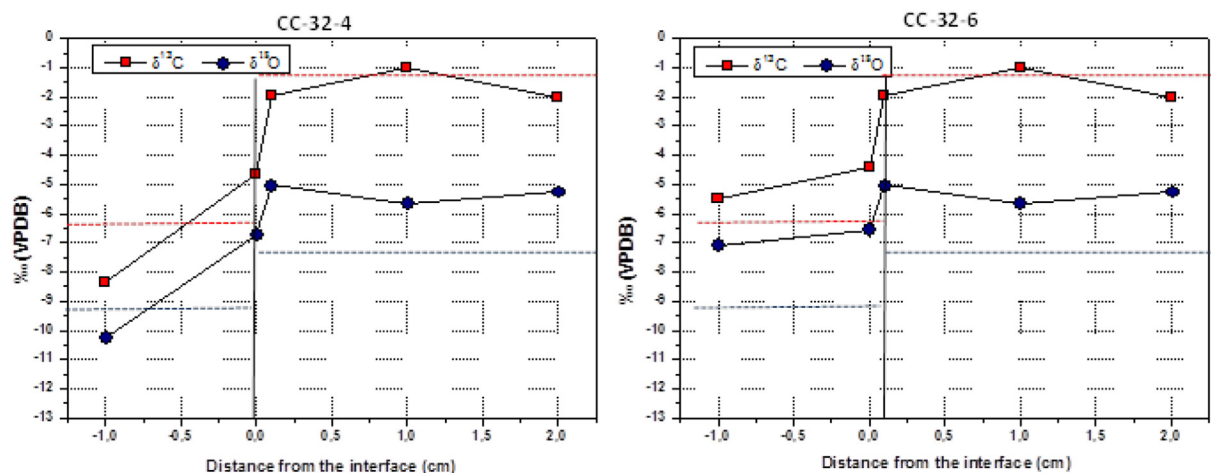


Fig. 9. Evolution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in the concrete-bentonite interface in samples CC-32-4 and CC-32-6.

mixing processes between formation groundwater, bentonite porewater and concrete leachates. Regarding oxygen isotopic composition, when secondary calcite is formed via dissolution/precipitation in meteoric water or groundwater, as in our case, the $\delta^{18}\text{O}_{\text{calcite}}$ should shift to lighter values. On the contrary, a secondary recrystallization of calcite in bentonite porewater would lead to heavier $\delta^{18}\text{O}_{\text{calcite}}$ values.

Spatial distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in the proximity of the contact between the concrete plug and the bentonite barrier shows significant variations of the isotopic signature in both, the concrete plug and the bentonite barrier (Fig. 10).

From the 3D-plotting of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values measured at both sides of the concrete-bentonite interface, the movement towards the concrete plug of a chemical front generated by bentonite leaching can be distinguished. In the contact with the concrete plug, the precipitation of the dissolved carbon in the formation groundwater together with this front would lead to the formation of secondary calcite depleted in ^{13}C due to the intense dissolution-reprecipitation processes enhanced by the leaching of bentonite. $\delta^{18}\text{O}$ values shift towards more negative

values in the outer areas of the concrete plug and the bentonite barrier, due to a greater exposition to groundwater formation. Besides, heterogeneous structure of the concrete plug and the existence of preferential pathways in the proximity of the interface favor non-homogeneous hydraulic behavior.

Newly-precipitated and/or recrystallized calcite carries the isotopic signature of the porewater in which it was formed. So, based on the $\delta^{18}\text{O}$ values measured for bentonite and concrete samples at both sides of the interface, an estimation of the isotopic signature of the concrete and bentonite porewater can be made.

$\delta^{18}\text{O}$ values calculated for the calcite formation porewaters are shown in Fig. 11 and Fig. 12. For ease of understanding, average $\delta^{18}\text{O}$ measured for Grimsel groundwater, bentonite porewater and bentonite leachates are displayed together with the calculated values. Calculations were performed by using eqs. (1)–(3). Depending on the sample location in the interface section, significant $\delta^{18}\text{O}$ variations are observed regarding the isotopic nature of the porewater. These differences point to the occurrence of mixing processes with variable contributions

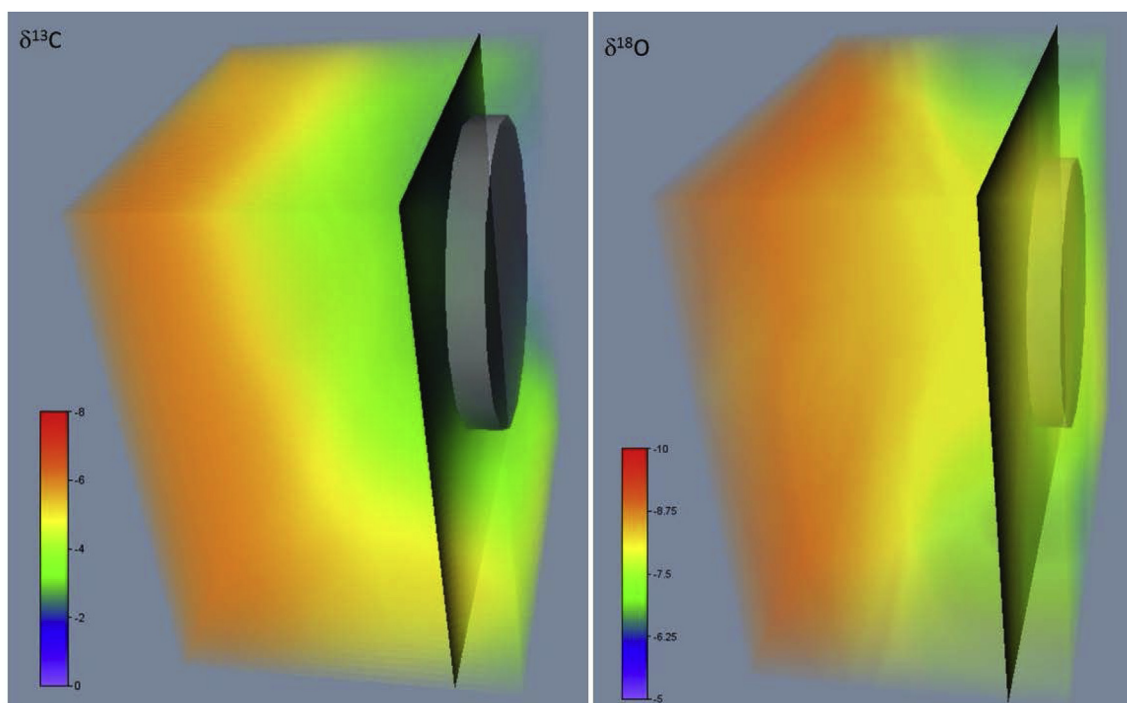


Fig. 10. Spatial distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in the proximity of the contact between the concrete plug and the bentonite barrier.

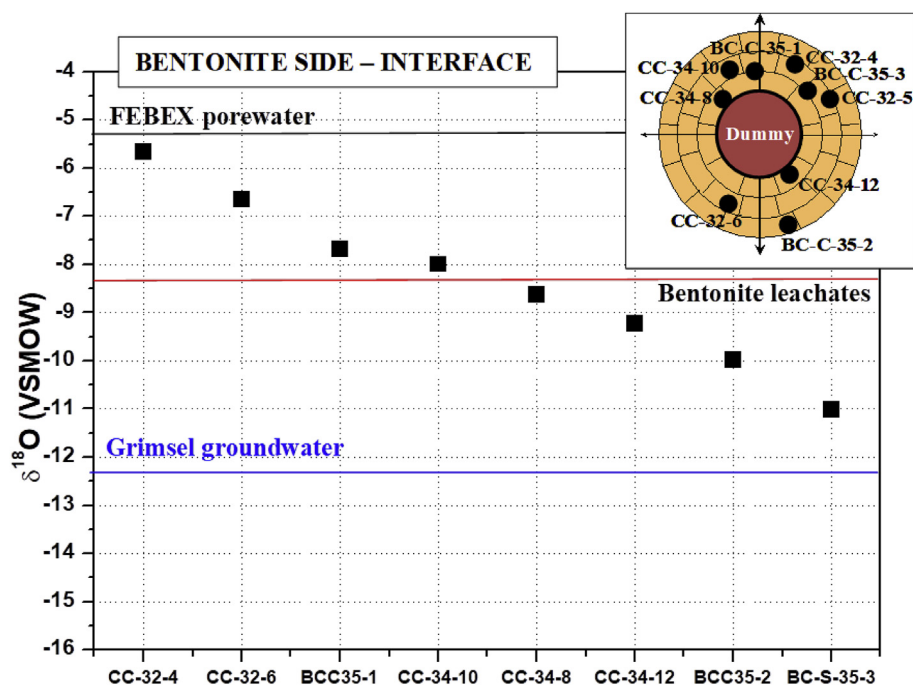


Fig. 11. $\delta^{18}\text{O}$ values calculated for the solution where calcite was formed in each of the studied samples in the concrete side in the interface.

of groundwater and bentonite leachates.

Enrichment in heavy isotopes of the porewater solution might possibly be related to the increasing influence of bentonite porewater. In concrete sampled at the interface, the alteration of calcite seems most likely induced by the migration of bentonite leachates into the concrete plug. In the case of bentonite, calculated $\delta^{18}\text{O}_{\text{solution}}$ points to significant differences depending on the location of the samples. These differences might be related to different degrees of exposure of each sample to bentonite porewater, groundwater and the concrete-bentonite leachates. A greater exposure to groundwater leads to more negative $\delta^{13}\text{C}_{\text{calcite}}$ values, whereas more positive $\delta^{13}\text{C}_{\text{calcite}}$ values correspond to bentonite less exposed to dissolution processes.

Comparison between Figs. 11 and 12 has allowed the grouping of

the different sampling points into three categories:

- Points with scarce bentonite leaching: influence by the chemical composition of bentonite porewater mainly at both sides of the interface: C-C-32-4 and C-C-32-6.
- Points with intense bentonite leaching, due to the existence of preferential pathways in the bentonite barrier and intense diffusive transport: C-C-34-8, BC-C-35-2, BC-C-35-3.
- Points in the concrete plug with a great exposition to formation groundwater, and limited leaching in the bentonite side: BC-C-35-1, C-C-34-12 and C-C-34-10.

The spatial distribution of carbon isotopic values in the concrete

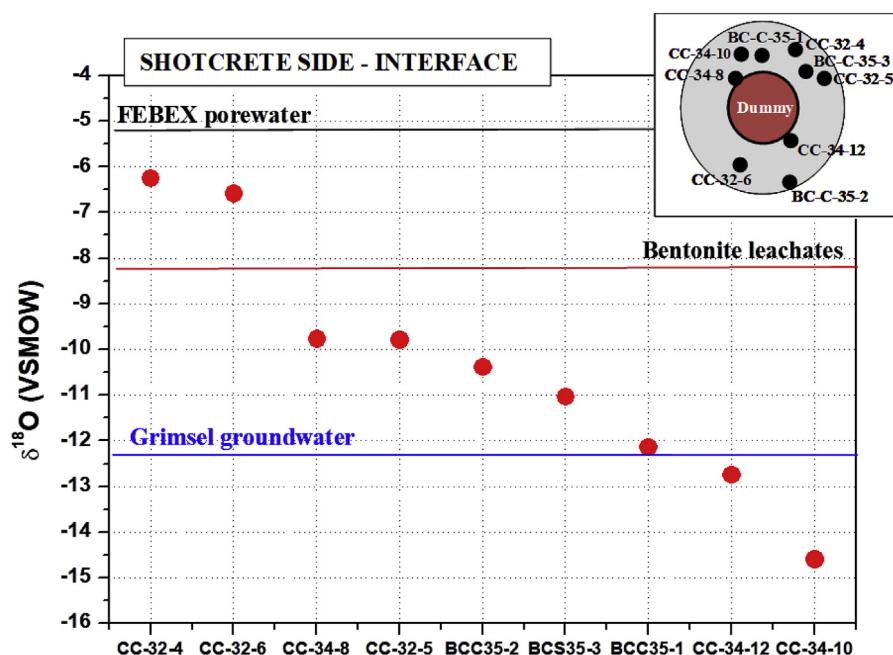


Fig. 12. $\delta^{18}\text{O}$ values calculated for the solution where calcite was formed in each of the studied samples in the bentonite side of the interface.

plug and the first centimeters of the bentonite barrier point to the existence of a diffusion front of carbonated species from bentonite towards the concrete plug (Fernández et al., 2017). Newly-precipitated and/or recrystallized calcite carries the isotopic signature of the porewater in which it was formed. The overall shift of the isotopic signature of bentonite in the interface towards more negative values near the interface, suggests the intrusion of formation groundwater through preferential pathways. The main reason is the heterogeneity of the concrete plug and the lower bentonite densities reached in the contact with the concrete plug. The greater exposition of the bentonite to formation groundwater, the more the bentonite is leached. The chemical front generated by bentonite leaching moves by diffusion in the saturated media and pH-sensitive chemical species such as Mg and carbonate precipitate when contacting alkaline fluids. Calcite dissolution and reprecipitation processes occurring in the interface lead to the depletion of ^{13}C and ^{18}O in neoformed calcite. This depletion occurs at different extends, depending on the nature of the contributions to the porewater where secondary calcite has been formed. As shown in Figs. 11 and 12, lower $\delta^{18}\text{O}$ values seem to be related to a greater groundwater contribution.

In the case of concrete samples, a greater exposition to formation groundwater would be expected in samples with calculated $\delta^{18}\text{O}$ values closer to the $\delta^{18}\text{O}$ of the groundwater. This would be related to the existence of preferential pathways through the plug. In the case of bentonite, samples with lower calculated $\delta^{18}\text{O}$ values would be greatly exposed to groundwater, which would favor the leaching and later, the diffusive transport of the dissolved chemical species towards the plug. The existence of this chemical front from the bentonite would modify the isotopic signature of the secondary calcite precipitated at the contact with concrete, leading to calculated $\delta^{18}\text{O}$ values close to the one measured for the bentonite leachates.

5. Conclusions

The monitoring of the FEBEX *in situ* experiment and the possibility of obtaining groundwater samples during the years of operation has made possible to know not only the baseline status but also the evolution of the system and the mass transfer processes. Both are important issues for the validation of reactive transport models.

The application of stable isotopes to study mass transfer (carbonates) in the concrete/bentonite interface points to a non-homogeneous chemical environment along the concrete/bentonite interface. The calculated $\delta^{18}\text{O}$ value of the solutions in which secondary calcite was formed seem to support significant differences depending on the location of the samples in the plug. Existence of preferential flow areas would be favoured by the proximity of the granite wall and the heterogeneity of the concrete-bentonite interface itself.

Spatial distribution of $\delta^{13}\text{C}$ values along the concrete plug and the first centimeters of the bentonite barrier points to the existence of a diffusion front of carbon species from bentonite towards the concrete-bentonite interface that induces the precipitation of calcite at the first millimetres of the concrete.

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