Supplementary Information for the article:

DIGIT: An In Situ Experiment for Studying the Diffusion of Water and Solutes under Thermal Gradient in the Toarcian Clay Rock at the Tournemire Underground Research Laboratory: Part~1---Goals, Scoping Calculations, Installation and First Results under Unheated Conditions

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Supplementary experimental section

S1. Elemental and speciation measurement for halogens

Anion measurements (Cl^-, Br^- and I^-) was carried out on filtered water samples using a Metrohm 930 Compact Ion Chromatography system. The chromatographic system was equipped with Metrosep C trap 1 (37-74 µm particle diameter 4 mm i.d. × 30 mm), Metrosep A Supp 19 guard column (5 µm particle diameter, 4 mm i.d. × 5 mm) coupled with a Metrosep A Supp 19 analytical column (5 µm particle diameter, 4 mm i.d. × 150 mm), a 250 µL PEEK injection loop (Methrom), a thermostatic column oven set at (35 ± 0.1) °C, a mobile phase containing 8 mmol L^{-1} Na_2CO_3 and 0.25 mmol L^{-1} $NaHCO_3$, a Metrohm MSM suppressor using regenerant solution containing 500 mmol L^{-1} H_3PO_4, and Metrohm conductivity detector. The flow rate of the mobile phase was fixed at 700 µL min^{-1}. Standard solutions were freshly prepared in deionized water from anions chromatography solution including Cl^-, Br^-, NO_3^-, NO_2^-, I^-, SO_4^{2-} and PO_4^{3-} (100 mg L^{-1}; conditioned in deionized water; CPAchem). The concentration range ranged between 0.01 and 10 mg L^{-1}. The detection limit of Cl^-, Br^- and I^- was the following: 5.3, 0.8 and 10 µg L^{-1}, respectively.

Total elemental concentrations (Br and I) were measured from filtered and basified samples using an Inductively Coupled Plasma – Tandem Mass Spectrometry (ICP-MS/MS; Agilent 8800) located at the IRSN's PATERSON platform. The spectrometer was run in MS/MS mode using H_2 at 5 ml min^{-1}; these operating conditions were employed to implement the possibility to measure simultaneously Cl, Br and I in a single run. The operating conditions can be found in Table S1. ICP-MS/MS spectrometer was calibrated using freshly standard solutions following a matrix-matching procedure between samples and standard solutions (*i.e.*, 300 mmol L^{-1} NH_3 for basified water samples). Internal standard (^{126}Te in 300 mmol L^{-1} NH_3) was used to correct for instrumental signal drift of ICP-MS/MS over time; the concentration of the internal standard concentrations was adjusted to obtain 40000 – 70000 cps at m/z 126. Standard solutions were prepared from anion chromatographic solution, and internal standard solution using Te (1g L^{-1}, 2 % HNO_3; VWR). The concentration range ranged between 0.1 and 50 µg L^{-1}. The detection limits for Br and I was 0.40 and 0.006 µg L^{-1}, respectively.

Speciation measurement was carried out in filtered water samples by chromatographic separation using a Metrohm 940 Professional IC Vario Ion Chromatography (IC) system. Separation of bromine (Br^- and BrO_3^-) and iodine (I^- and IO_3^-) was performed using Metrosep A Supp 10 guard column (4.6 µm particle diameter, 2 mm *i.d.* × 5 mm) coupled with a Metrosep A Supp 10 analytical column (4.6 µm particle diameter, 2 mm *i.d.* × 250 mm), a 20 µL PEEK injection loop, a thermostatic column oven set at (35 ± 0.1) °C and a PEEK capillary (15 cm) connecting the column outlet to the nebulizer of ICP-MS/MS (parameters in Table S1). The flow rate of mobile phase was fixed at 250 µL min^{-1}. Ammonium nitrate (NH_4NO_3) was chosen as mobile phase due to its best compatibility with ICP-MS measurement and the capacity of NO_3^- to elute the target species in ternary ammonium-based stationary phase. Its concentration was 50 mmol L^{-1}, the same chromatographic conditions employed in *[45]*. Standard solutions were freshly prepared in deionized water from anions chromatography solution including Cl^-, Br^-, NO_3^-, NO_2^-, I^-, SO_4^{2-} and PO_4^{3-} (100 mg L^{-1}; conditioned in deionized water; CPAchem), mono-anion standards of BrO_3^- and IO_3^- (1 g L^{-1}; conditioned in deionized water; VWR). The tests were conducted using radial diffusion cells on samples from the reference borehole DGT-REF at a depth of 276 cm. An example of speciation controls for Br and I display Figure S1.

Supplementary Table

Table S1. ICP-MS operating conditions.

Analytical parameters	Value/description
Sample introduction system	
Nebulizer	PFA concentric nebulizer (ESI)
Torch	PFA demountable torch with a sapphire injector
Spray chamber	Double-pass PFA spray chamber cooled at 2 °C
Internal standard connection	PFA T-piece
Carrier gas flow	1 l min^{-1}
Makeup gas flow	0.23 l min^{-1}
Type of cônes	Ni cones
ICP-MS conditions	
Sample depth	7 mm
RF power	1600 W
Plasma gas flow rate	15 l min^{-1}
Auxiliary flow rate	0.9 l min^{-1}
Extract 1 and 2	−100 and −200 V
MS/MS mode	On mass
Monitored ions (Q1→Q2)	$^{79}Br^{+}$→$^{79}Br^{+}$, $^{127}I^{+}$→$^{127}I^{+}$, $^{126}Te^{+}$→$^{126}Te^{+}$
Background signal (0.3 mol l^{-1} NH_3)	≈ 500 cps at m/z = 79→79 and 127→127
Sensitivity	20,000 and 120,000 cps for 10 μg l^{-1} of Br and I, respectively
Rinse time (0.3 mol l^{-1} NH_3)	2 × 45 s
Rinse flow rate	0.5 rps
Acquisition parameter	
Integration time	0.5 s
Peak shape	1 point
Number of sweeps per replicate	50
Number of replicates per sample	5

Supplementary Figure

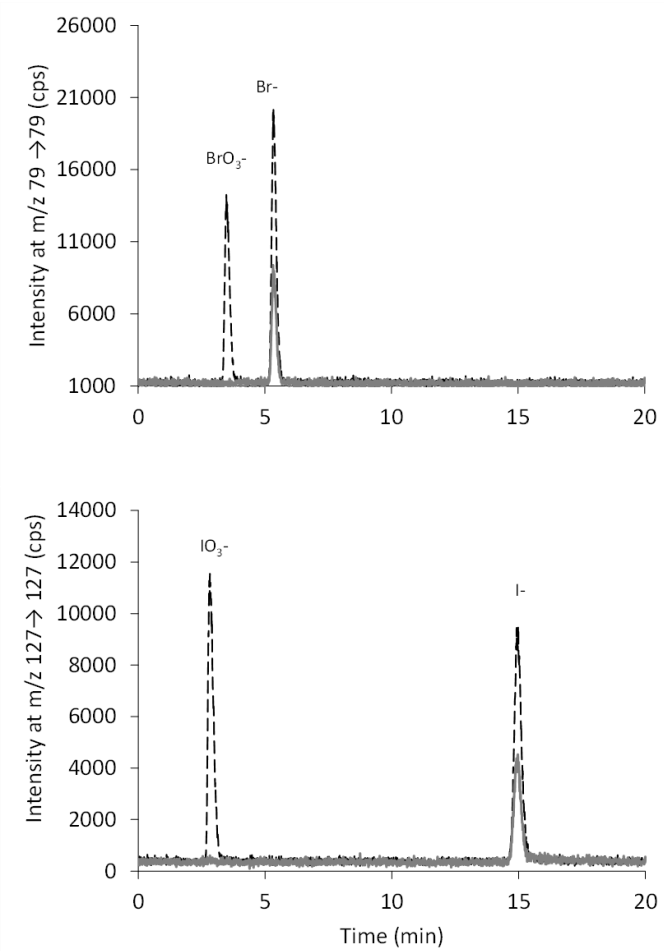

Figure S1. Example of chromatogram obtained for filtered samples grey line) and compared to standard solutions (doted black line) whose the concentrations of bromine and iodine species were 20 and 1 μg l^{-1}, respectively. Note that nonorganic Br and I species were found during speciation controls.