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Evaluation of a Long-Term Thermal Load on the Sealing Characteristics of Potential Sediments for a Deep Radioactive Waste Disposal

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Abstract: An in situ and a batch heating experiment were applied on the fine-grained sediments of the Opalinus Clay from Mont Terri (Switzerland) and the Boom Clay of Mol (Belgium), both being currently studied as potential host formations for deep nuclear waste disposal. The purpose was here to test the impact of a 100 °C temperature rise that is expected to be produced by nuclear waste in deep repositories. The experiment on the Opalinus Clay mimicked real conditions with 8-months operating heating devices stored in core drillings into the rock. The comparison of the major, trace, rare-earth elemental contents and of the whole-rock K-Ar data before and after heating shows only a few variations beyond analytical uncertainty. However, the necessary drillings for collecting control samples after the experiment added an unexpected uncertainty to the analyses due to the natural heterogeneity of the rock formation, even if very limited. To overcome this aspect, Boom Clay ground material was subjected to a batch experiment in sealed containers during several years. The drawback being here the fact that controls were limited with, however, similar reproducible results that also suggest limited elemental transfers from rock size into that of the <2 μm material, unless the whole rocks lost more elements than the fine fractions. The analyses generated by the two experiments point to identical conclusions: a visible degassing and dewatering of the minerals that did not induce a visible alteration/degradation of the host-rock safety characteristics after the short-term temperature increase.

Keywords: long-term heat experiments; fine-grained sediments; deep disposal of nuclear waste; major; trace and rare-earth elements; K-Ar tracing; Opalinus Clay; Boom Clay formations

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1. Introduction

Petrophysical, mineralogical and geochemical studies of deep-seated geological sediments that might be selected as host formations for nuclear waste disposal require careful controls of their safety characteristics. In order to check these conditions, specific experiments were designed and performed in dedicated experimental underground laboratories. The data generated during such experiments need to be as representative as possible of the intrinsic characteristics of the target rocks before any human interference. The challenge is then the completion of reference analyses and observations as representative as possible of the original intact rocks.

In this context, appropriate drilling techniques were used in and around the Mont-Terri rock-laboratory to minimize the exchange reactions between the compositional minerals of the drilled rocks and the incoming atmosphere. However, despite all the care taken during such drillings and the conditioning under vacuum of the core pieces, the sampled material underwent various alteration reactions [1,2]. Oxidation by contact with the atmosphere resulted from almost instantaneous supply of O_2, CO_2 and water to rocks that were confined in reduced conditions with very limited amounts of fluids and gases for millions of years. Local disturbances can also occur by an instantaneous dehydration due to temperature increase, for instance during coring, possibly followed by some rehydration depending on how the recovered samples were handled, or on the conditions applied to the excavated sites. It has already been shown, in this context, that deeply buried sediments excavated for shafts and galleries yield modifications on their walls that were called "excavated damaged zones" (labeled EDZ hereafter) and "excavated disturbed zones" (EdZ) [3–9]. Horseman [10] suggested even that this recent evolution in the stress path also leads to a reduction in the permeability of the sediments.

The present study was designed in this context to evaluate analytically the impact of a long-lasting heating experiment on the geochemical and mineralogical signatures of host formations and more precisely on the sealing potential of rocks immediately around containers that are expected to release spontaneously heat due to the nuclear waste itself. The purpose was not to construct a model based on theoretical hypotheses, but to identify and quantify the changes on the basis of factual analyses. Indeed, mathematical models elaborated specifically for deep-disposal of nuclear waste are already available based on the fact that the storage will induce a moderate but extremely long-lasting temperature increase on the host rocks (e.g., [11,12]). As the spontaneous heat produced by the radioactive waste on its immediate environment has already been modeled, analytical controls of such an impact on the immediate environmental host rocks are now needed to check and consolidate these models. The present study is based on two experiments to evaluate such an impact of a long-term artificial heating: (1) on the Aalenian-Toarcian (183–170 Ma) Opalinus Clay Formation (called OPA hereafter) at the Mont Terri in Switzerland where an in situ experiment called HE-D was completed, and (2) on the Rupelian (34–28 Ma) Boom Clay Formation at Mol in Belgium, which was subjected to a batch experiment during 7 years at an ambient temperature of 80 °C. The reason for combining two different heating experiments on two different sedimentary formations is because the analytical controls of the OPA rocks after the experiment needed a supplementary coring to obtain the heated samples. In turn, as even very close samples can be slightly different in their mineralogy and chemistry, some of the possible analytical differences may be due to the sample mineralogy and not to the heating experiment. This aspect was not of concern in the case of the batch experiment as the same samples were analyzed along a "closed" experiment. However, the number of controls had to remain limited because each needed the opening of a container, which was lost for the continuation of the experiment.

2. Description of the Experiments, the Sampling and the Analytical Methods

2.1. The In Situ Experiment in the Opalinus Clay of the Mont-Terri Rock Laboratory

The in situ heat experiment was based on the study of the 8-m long BHE-D0 borehole drilled into the OPA from HE niche of the so-called 'new gallery' in the rock laboratory (Figure 1). The concept was heating the clay formation at a steady temperature in an undisturbed zone with no protecting backfill material around two heating devices inserted into the borehole. The mineralogical and geochemical characteristics of the drilled sequence were examined as references before heating on five samples collected along a second borehole BHE-D5 drilled perpendicularly to the BHE-D0 borehole from nearby MI niche through the EDZ and the unsaturated zone of the niche, both zones being considered to be about 1 m and 1.5 m thick, respectively [13,14]. During the initial 3 months, the two heaters in BHE-D0 borehole were set to diffuse a progressive heat flux from 15 °C to 43 °C and, then, to propagate a temperature of 100 °C during 8 months. After these 8 months of heating, 9 more months were allowed for the cooling of the rocks before collection, by drilling, of the 'heated' samples, close to and far from heaters. This sampling was completed along the BHE-D5 borehole and along a second BHE-D26 borehole cored parallel to the previous one (Figure 1). The samples from beyond the identified EDZ and EdZ zones were stored 8 more months under vacuum, before analysis. Those of these EDZ and EdZ volumes were analyzed previously in a study dedicated to the ‘aging’ effect after a regular excavation of galleries and niches [2].

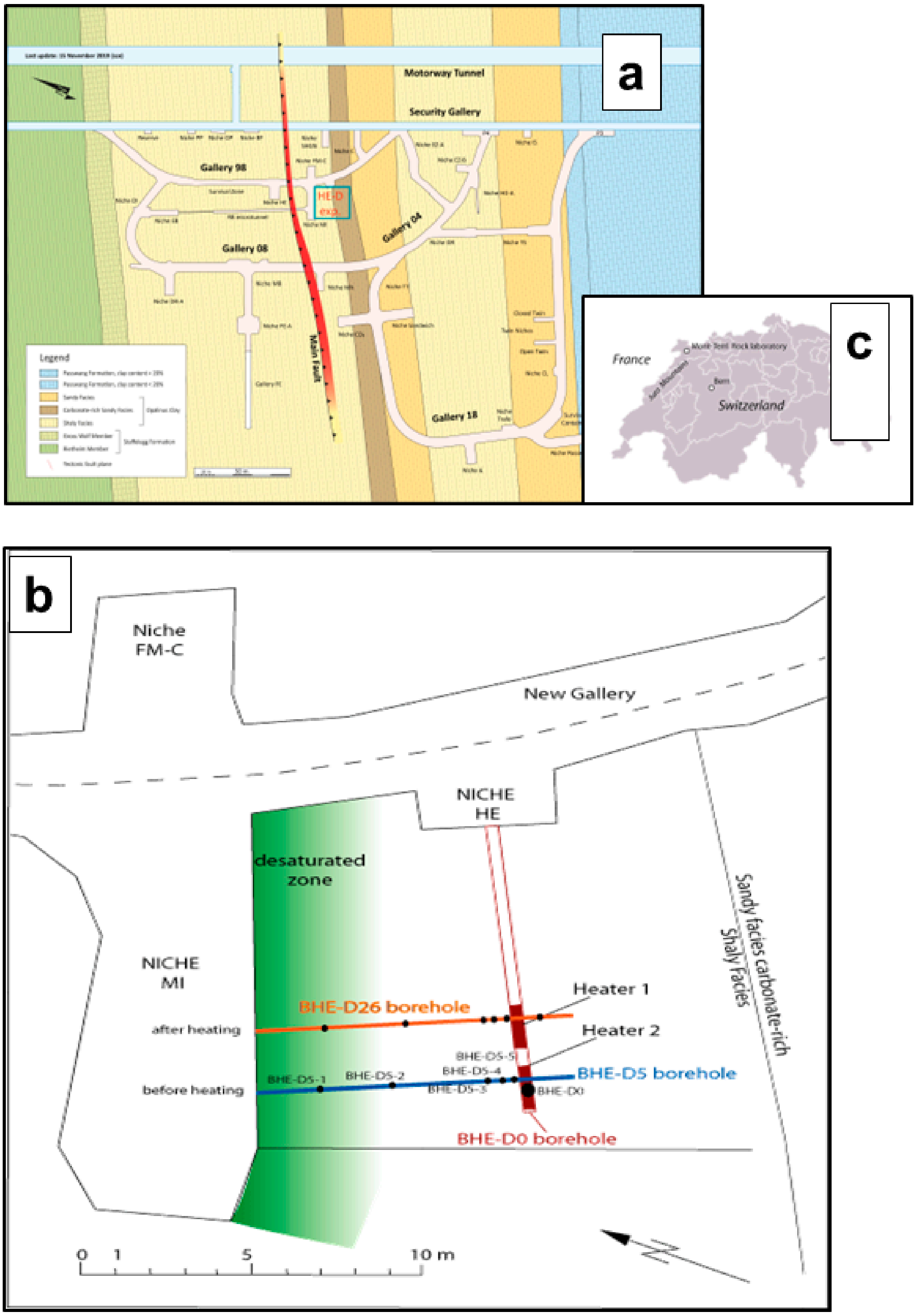


Figure 1. (**a**) Location of the HE-D experiment in the Opalinus Clay of the Mont Terri rock laboratory; (**b**) A closer view of the experiment in the MI niche with the different drill holes; (**c**) The geographic location of the rock laboratory in Switzerland.

The 14 to 21 cm long samples collected before the heating experiment along the BHE-D5 borehole between 2.24 and 8.00 m from heater and at the tip of the BHE-D0 borehole were also stored under vacuum after recovery. After 11 months of heating and 9 months of cooling, six samples were collected perpendicularly to borehole BHE-D0 at an increasing distance from heaters, as well as along the BHE-D26 borehole drilled after heating in the same rock volume. To keep the collected volume as small as possible and to allow the after-heat sampling to be as close as possible to that before heating for most reliable comparisons, micro-cores of 25 mm in diameter were drilled into each of the selected samples for the planned mineralogical, chemical and isotopic analyses.

2.2. The Batch Experiment of the Boom Clay

The main objective of the longer batch experiment completed on ground Boom Clay rocks under closed conditions at 80 °C during several years (Figure 2) was a precise analysis of the released CO_2 gas yields during heating of potential host material in the conditions of a deep waste disposal (e.g., [15–17]). Analyses were carried out on whole rocks and <2 µm-sized residues after dismantling of a batch container at each controlling step. The initial gas pressure was set at 20 bars and was controlled by pressure sensors connected to the pressure vessels with Ar as the cushion gas. The complete experiment lasted 2529 days with an opening for sample collections of two containers after 830 and 1799 days. The initial rock sample and its <2 µm fraction, and those from the two intermediate steps were analyzed, before and after an additional leaching with dilute (1M) hydrochloric acid, for the major, trace and rare-earth elements (REEs) and for the K-Ar isotopic systematics to which a special attention was given about the desorption of the atmospheric Ar used during the experiment as the cushion material.

Figure 2. View of the long-term batch experiment on the Boom Clay rock ships at 80 °C.

2.3. The Analytical Methods

All samples collected for the two experiments were observed by scanning electron microscope (SEM) and then were crushed gently, a powder aliquot of each being taken for their mineralogical, chemical and isotopic analyses. For the Boom material, the samples were subjected to quantitative X-Ray diffraction (XRD), were mixed with 10 wt% of ZnO as an internal standard, and milled in methanol for 5 min in a McCrone Micronizing Mill. Then, the powder was scanned on a Bruker D8 instrument equipped with a CuKα radiation and a Bruker LynxEye detector (Bruker, Billerica, MA, USA). The obtained spectra were analyzed by the Profex 4.3.2 release [18] and the BRGM mineral database. The XRD analyses of the OPA material were completed on a Bruker D5 instrument with the same radiation, but no LynxEye detector and no special quantification program. Still for the Boom Clay, the recovered rock powder was settled in distilled water for a classical separation of the <2 µm size fraction by sedimentation following the classical Stokes' law. The smeared <2 µm specimens were XRD analyzed two times in an air-dried and ethylene-glycol state on a Philips PW1830 diffractometer with a CuKα radiation and a PW3011/00 proportional detector. In turn, the obtained data of the clay minerals were similar to those described by Zeelmaekers et al. [19] and Frederickx et al. [20]. The leachates of the rocks and size fractions were also analyzed for their major, trace and rare-earth elements by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), following the procedure of Samuel et al. [21]. The reproducibility and accuracy tests of the BE-N and GL-O international standards gave recommended values for the contents with standard deviations better, on the basis of 9 independent runs during the time of the analyses, than the given average of 2.5% for the major elements, 4.5% for the trace elements and 10% for the rare-earth elements (REEs).

To constrain best the chemical and mineral variations due to heating and, therefore, the amounts of the mobilized elements, some of the collected samples were also leached with dilute (1M) hydrochloric acid during 15 min at room temperature. After leaching, the mixtures were centrifuged and the leachates evaporated and analyzed for their chemical compositions by ICP-AES and/or by ICP-MS. The K-Ar procedure applied to the fresh and heated samples and to some <2 µm fractions is similar to that presented by Bonhomme et al. [22]. The Ar extractions were completed in a glass line coupled directly with the gas mass-spectrometer; a preliminary degassing at 80 °C during 24 h being systematically applied to remove any adsorbed atmospheric during the sample preparation. Potassium was measured by atomic absorption with an accuracy of ±1.5%, which was controlled by periodic analysis of the same B-EN and GL-O international standards. The quality of the Ar extractions was controlled by a weekly analysis of the standards, as well as of the atmospheric $^{40}Ar/^{36}Ar$ ratio and the blank of the extraction line coupled to the mass spectrometer. There was no need for data corrections as the average content of the radiogenic ^{40}Ar from GL-O standard and the atmospheric $^{40}Ar/^{36}Ar$ ratio were close to the theoretical values at 24.57 ± 0.60 (2σ) cm^3/g [23] and 298.6 ± 0.4 (2σ) [24], respectively. The blanks of the gas line and the gas spectrometer were also far below the measured contents of the samples. The usual decay constants were used for the age calculations [25] with an overall error of the K-Ar age determinations better than 2%.

3. Results

3.1. The Characteristics of the Reference Opalinus Clay Material

Previous XRD data gave a classical shaly composition for the OPA sediments [26,27]. Here, the samples appeared quite homogeneous along the 8 m long profile at the SEM scale. However, observations of pyrite that represents a potential mineral sensitive to heating and external air supply, showed some discrete changes, even before the heating experiment. In most samples from cores drilled for the emplacement of the heaters, pyrite occurs either as visually 'clean' framboïdal aggregates or large individual minerals, as for instance in sample BHE-D5-1 collected 7 m away from heater (Figure 3A). About 2.1 m away, and still before the heating experiment, some of the framboïds appear slightly erased and 'polished' (Figure 3C). After the 8 months heating experiment, the pyrite crystals at 5.6 m from heater were covered by a veil that looks as it has been torn somehow (Figure 3B), while the surficial crystals of the aggregates appeared altered and even peeled off with a pristine central core at 2.0 m from heater (Figure 3D). These modifications suggest some alteration by oxidation of the aggregated or the individual pyrite crystals, even before the heating experiment. Janots et al. [28] related similar veils to the activity of sulfate reducing bacteria, which action could have started right after drilling of the core due to an atmospheric/bacterial contamination that could have been amplified by the heating experiment.

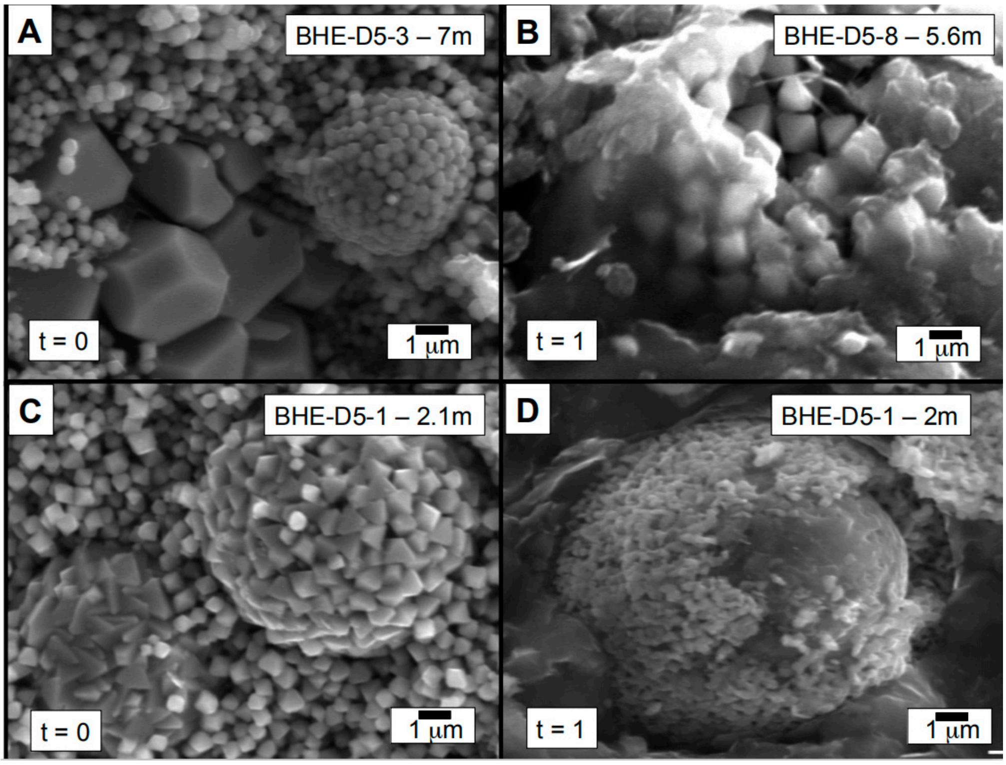


Figure 3. SEM pictures of pyrite crystals and agglomerates from OPA sediments. The sample identifications are in the photographs, as well as the locations, the timing (t = 0 means before heating and t = 1 means after heating) and the scale (modified from Techer et al. [2]). (**A**) Picture of large pyrite and aggregated minuscule pyrite crystals before heating; (**B**) the same small crystals wrapped in a veil after heating; (**C**) an enlargement of the pyrite crystal balls before heating; (**D**) the same kind of crystal ball after heating.

Before heating, the major elements from reference rocks along the BHE-D5 drilling vary only slightly, except an increase in the loss on ignition (LOI) when sampling approaches the MI niche. This change corresponds probably to the above-identified EDZ/EdZ that was exposed to atmosphere during the excavations of the gallery and the niche. While most major elemental contents appear quite constant towards the heater before the experiment, there is a clear decrease in the CaO content towards the EDZ/EdZ zone of the niche, together with a decrease of the SiO_2 content (Table 1, Figure 4). This decrease in Ca changes into ups and downs after heating, while the contents of the other elements remain quite stable. The changing Ca of the rocks along the collection trend suggests discrete natural mineral heterogeneities due to how the samples were collected and stored after heating. They were taken as close as possible to the initial samples, as it could not be done differently, which does not guarantee a strict mineral and, therefore, a strict chemical identity. This weakness had to be kept in mind, while comparing the chemical data of the samples collected before and after the heating experiment. In this context, the analytical aspect of very uniform total contents of the major elements around 100% for the sums of the analyzed major elements is of importance for overall mineral and chemical uniformities, confirming also an analytical reproducibility better than the routinely assumed ±2.5% uncertainty. In sum, it is plausible that some of the changing elemental contents result from a discrete heterogeneity in the mineral compositions due to the additional drillings rather than to the long-term heating. In the case of the trace elements, the Sr contents increase significantly towards the niche and therefore away from heater, while those in Zr, Zn and Cu decrease, but to a lesser extent. For all other elements, the contents remain quite homogeneous, again beyond the EDZ and EdZ zones (Figure 5). In fact, the slight changes along the profile from heater to the MI niche wall decompose into a fair steady content between

2 to 7-m away from the niche wall, except for Si and Ca, and Sr, Ba and Y. The scatter becomes larger beyond 7 m away from the wall, which could be due to already reported lithological variations in the shaly OPA facies [26,27]. Significant elemental variations were also detected in the analyses of the soluble mineral phases of the samples recovered by a gentle leaching with dilute hydrochloric (1M) acid during 15 min at room temperature (Table 2). Indeed, the leachates become clearly enriched in Si, Al and K, while Mg, Fe, Na and P remain quite stable, and Ca is significantly depleted close to the MI niche before heating in the EDZ/EdZ zone.

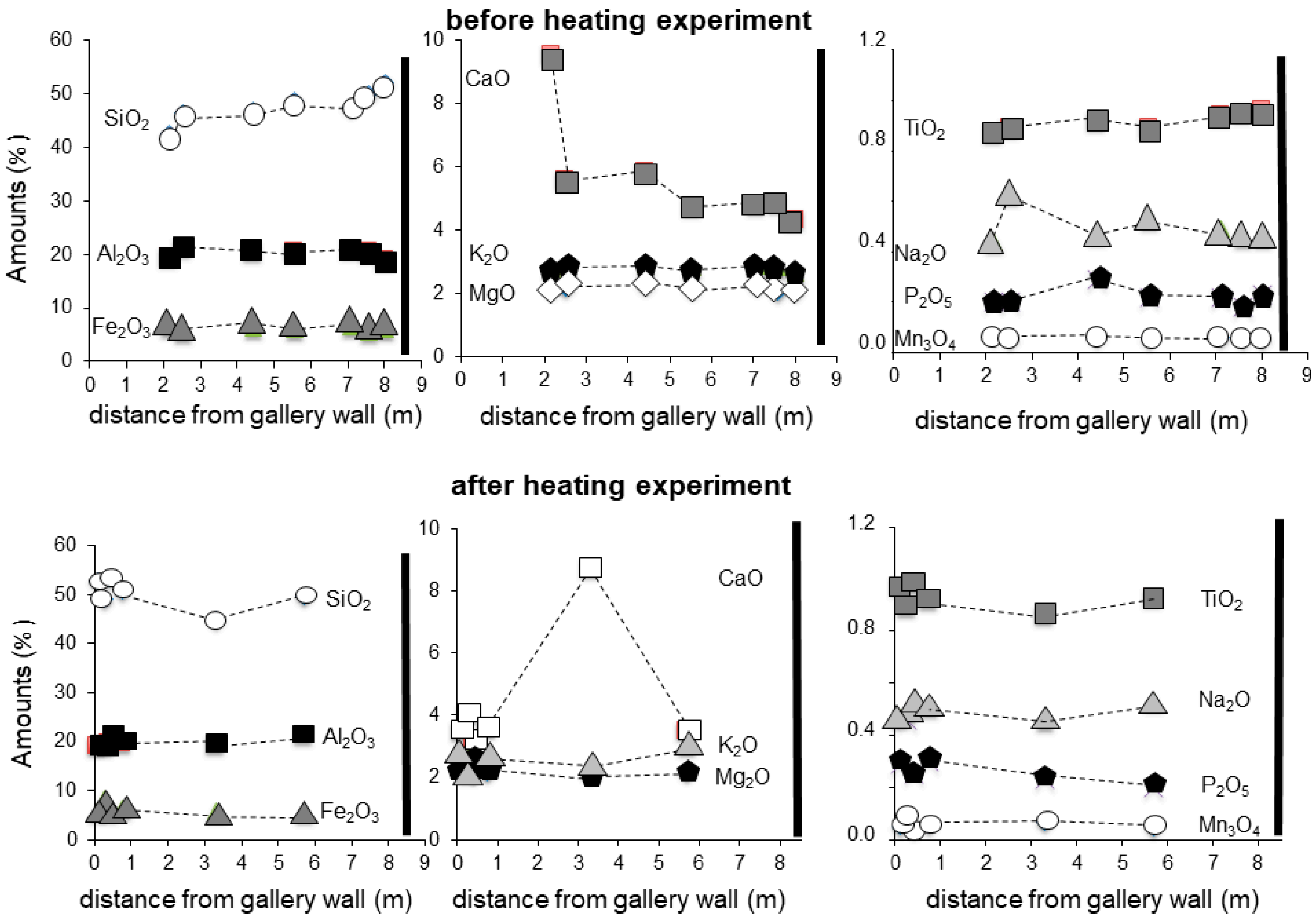


Figure 4. Variations of the major elements from OPA whole rocks during the heating experiment. The thick bar to the right represents the heater.

Table 1. The major and trace elemental contents of the OPA whole-rocks before and after the heating experiment.

Sample IDs	Place/MI Niche (m)	SiO_2 (%)	Al_2O_3 (%)	MgO (%)	CaO (%)	Fe_2O_3 (%)	Mn_3O_4 (%)	TiO_2 (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	LOI (%)	Total (%)	Sr (mg/g)	Ba (mg/g)	Rb (mg/g)	Pb (mg/g)	Th (mg/g)	U (mg/g)
initial																			
BHE-D5 0	8.00	50.7	20.6	2.27	3.47	6.54	0.052	1.01	0.79	3.06	0.24	11.32	100.1	201	302	133	23.9	13.9	3.00
BHE-D5 5	7.96–8.15	52.0	18.8	2.10	4.30	5.94	0.054	0.96	0.46	2.63	0.23	11.56	99.12	216	291	65.4	14.6	8.46	1.85
BHE-D5 4	7.50–7.66	49.9	20.4	2.05	4.84	5.56	0.054	0.95	0.46	2.81	0.18	12.08	99.28	217	282	68.8	14.5	8.50	1.94
BHE-D5 3	7.00–7.21	47.4	21.0	2.27	4.79	6.63	0.060	0.94	0.49	2.87	0.22	12.79	99.52	239	306	74.8	13.8	8.37	1.87
BHE-D5 2	4.36–4.50	46.8	20.5	2.24	5.83	6.31	0.059	0.92	0.47	2.92	0.29	12.91	99.31	282	281	76.2	13.6	8.32	1.83
BHE-D5 1	2.10–2.24	42.5	19.5	2.11	9.52	6.59	0.068	0.87	0.44	2.76	0.20	14.72	99.24	282	267	70.4	12.1	7.30	1.64
BHE-D5 8	5.50–5.60	48.7	20.5	2.13	4.72	6.00	0.056	0.89	0.53	2.83	0.22	12.17	98.79	209	367	129	28.3	12.8	2.82
BHE-D5 6	2.45–2.60	46.4	21.2	2.15	5.56	5.43	0.055	0.89	0.63	2.88	0.20	13.38	98.78	258	349	133	36.6	13.2	2.87
after heating																			
BHE-D26 2	5.70	49.7	21.2	2.15	3.50	5.42	0.046	0.93	0.53	3.04	0.20	11.48	98.22	222	287	153	46.4	15.6	3.47
BHE-D26 3	3.30	44.9	19.2	2.13	8.70	5.82	0.069	0.86	0.46	2.30	0.23	13.92	98.62	258	271	123	34.1	12.4	2.70
BHE-D26 8	0.75	50.7	19.7	2.15	3.57	6.40	0.056	0.92	0.51	2.62	0.30	11.54	98.41	198	279	136	43.2	16.1	3.29
BHE-D26 14	0.40	53.3	19.5	2.10	3.20	5.69	0.041	0.98	0.53	2.95	0.25	10.80	99.32	198	290	124	48.0	14.2	2.93
BHE-D26 10	0.27	49.0	19.0	2.42	4.00	8.20	0.070	0.89	0.49	2.14	0.46	12.21	98.95	205	261	108	38.8	12.5	2.64
BHE-D26 12	0.10	52.7	19.0	2.20	3.50	5.88	0.050	0.97	0.47	2.63	0.29	11.26	98.94	193	284	117	37.8	13.5	2.75

IDs stand for identities.

Table 2. The major and trace elemental contents of the OPA whole-rock leachates by dilute acid before and after the heating experiment.

Sample IDs	Place/MI Niche (m)	Si (µg/g)	Al (µg/g)	Mg (µg/g)	Ca (µg/g)	Fe (µg/g)	Na (µg/g)	K (µg/g)	P (µg/g)	Sr (µg/g)	Ba (µg/g)	Rb (µg/g)	Th (µg/g)	U (µg/g)
initial														
BHE D5 5B	7.96–8.15	7.27	15.1	9.05	374	6.45	29.6	15.5	0.29	1.17	0.04	13.8	8.12	1.43
BHE D5 4B	7.50–7.66	8.25	16.4	9.62	429	7.10	31.5	16.8	0.10	1.28	0.05	15.0	8.41	1.48
BHE D5 3B	7.00–7.21	7.79	13.4	9.29	403	6.15	33.3	16.7	0.31	1.41	0.05	15.9	9.93	1.97
BHE D5 2B	4.36–4.50	7.69	13.8	11.2	557	7.94	37.9	18.2	0.38	2.02	0.06	16.1	11.9	2.43
BHE D5 1B	2.10–2.24	1.26	2.54	9.32	691	7.44	34.9	6.25	0.25	1.67	0.02	6.23	11.1	2.09
after heating														
BHE D5-8	5.50–5.60	1.29	2.61	7.69	282	3.11	25.7	4.40	0.29	0.88	0.02	3.91	6.52	1.00
BHE D5-6	2.45–2.60	0.97	2.24	7.25	282	3.09	21.8	3.85	0.16	0.96	0.01	4.12	5.00	0.94
BHE D5-7	1.90–2.00	0.46	1.24	5.54	310	3.22	15.7	2.44	0.05	0.66	0.01	2.57	6.60	1.11

IDs stand for identities and m for meters.

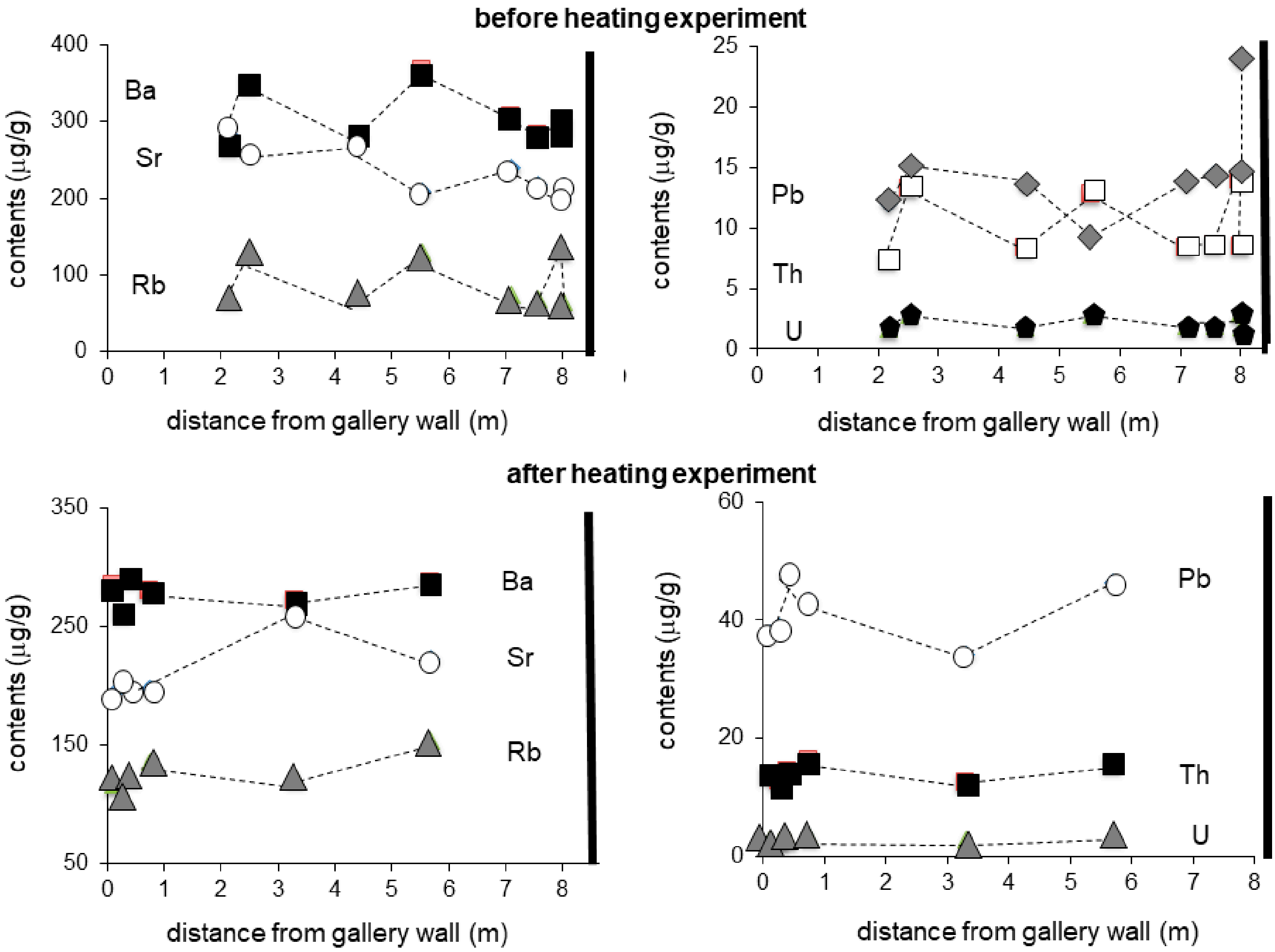


Figure 5. Variations of the trace elements from OPA whole rocks during the heating experiment. The thick bar to the right represents the heater.

The REEs yield specific characteristics including a strong ionic bond making them behave as strong acids [29]. Most occur generally with three electrons removed from three orbitals, while Eu and Ce behave differently: the former yields a half-filled orbital allowing a stability for the Eu^{2+} species and the latter yields an oxidation-reduction state allowing Ce to occur as either Ce^{3+} or Ce^{4+} [30]. As the amounts of the REEs in minerals are naturally quite dispersed among each other, their contents are often compared to those of international standards such as the North American Shale Composites (NASC) used here [30]. The widely dispersed REE contents of any kind of sample are then narrowed and easier to decrypt. Before heating, the REE patterns of the OPA rocks displayed, here, a decreasing slope from light REEs (LREEs) towards the heavy REEs (HREEs) (Table 3, Figure 6). The contents are also systematically depleted relative to the NASC reference, with an analytically significant positive Dy anomaly and a systematic increase of the Yb and Lu contents. To be also mentioned is the spectrum of the sample from EDZ/EdZ volume that is similar to those of the other samples.

Table 3. The rare-earth elemental contents of the OPA whole-rocks before and after the heating experiment.

Sample IDs	Location/ Probe (m)	La (µg/g)	Ce (µg/g)	Pr (µg/g)	Nd (µg/g)	Sm (µg/g)	Eu (µg/g)	Gd (µg/g)	Tb (µg/g)	Dy (µg/g)	Ho (µg/g)	Er (µg/g)	Tm (µg/g)	Yb (µg/g)	Lu (µg/g)	Total (µg/g)
initial																
BHE-D5/5	7.96–8.15	26.4	52.5	6.16	22.9	4.36	0.90	3.40	0.56	3.09	0.69	1.74	0.26	1.74	0.28	125.0
BHE-D5/4	7.50–7.66	27.5	52.4	5.96	20.7	3.83	0.75	2.88	0.48	2.87	0.63	1.68	0.25	1.69	0.27	121.9
BHE-D5/3	7.00–7.21	25.0	47.9	5.69	20.2	3.90	0.81	2.92	0.48	2.75	0.57	1.48	0.22	1.42	0.24	113.6
BHE-D5/2	4.36–4.50	27.1	55.8	6.57	24.4	4.81	0.95	3.65	0.60	3.25	0.67	1.70	0.24	1.59	0.26	131.6
BHE-D5/1	2.10–2.24	24.5	49.8	5.53	19.8	3.68	0.70	2.83	0.46	2.55	0.53	1.44	0.21	1.39	0.22	113.6
after heating																
BHE-D5/8	5.50–5.60	44.4	86.2	9.95	36.0	6.62	1.37	5.29	0.78	4.78	1.02	2.58	0.40	2.50	0.40	202.3
BHE-D5/6	2.45–2.60	46.3	93.0	10.5	37.7	7.11	1.51	5.48	0.84	5.04	1.04	2.74	0.43	2.62	0.42	214.7
BHE D26-14	0.4	46.6	92.7	10.5	38.3	7.16	1.48	5.78	0.85	5.16	1.10	2.79	0.44	2.86	0.45	216.2
BHE D26-12	0.1	44.7	91.2	10.7	39.7	7.68	1.57	6.38	0.89	5.39	1.11	2.89	0.45	2.78	0.44	215.9
BHE D26-10	0.27	43.4	96.3	11.8	46.3	9.51	2.01	7.63	1.09	6.10	1.23	3.01	0.45	2.67	0.42	231.9
BHE D26-8	0.75	53.0	107	12.4	45.8	8.83	1.86	7.10	1.00	6.19	1.29	3.32	0.52	3.11	0.49	251.9
BHE D26-3	3.3	42.1	81.4	9.12	33.6	6.10	1.29	4.94	0.72	4.28	0.94	2.43	0.37	2.42	0.36	190.1
BHE D26-2	5.7	48.7	96.2	10.8	39.4	7.46	1.53	5.71	0.86	5.18	1.13	2.81	0.46	2.78	0.45	223.5

ID stands for identities and m for meters.

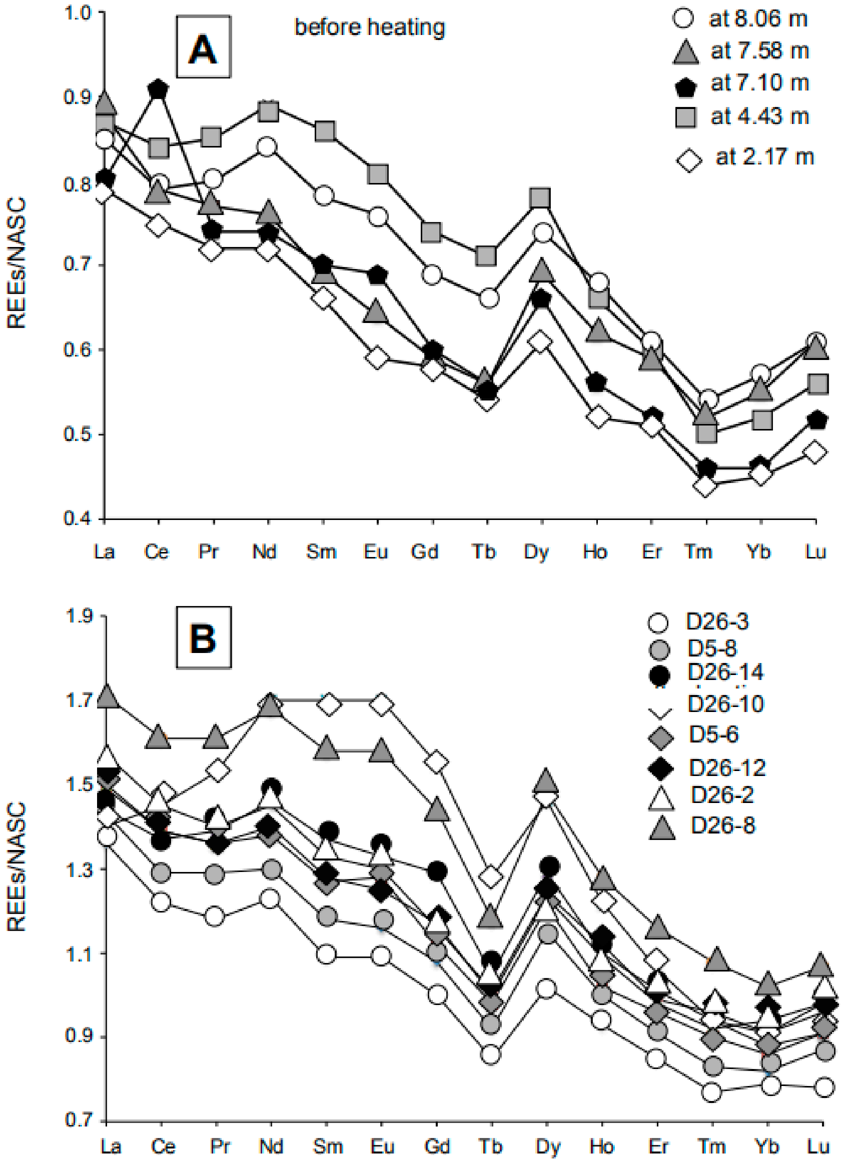


Figure 6. (**A**) The REE distribution patterns of the OPA whole rocks relative to the NASC reference at various distances from heater before the heating experiment; (**B**) the same after the heating experiment.

The K and Ar contents give K-Ar age values, with the isotopic ^{40}Ar/^{36}Ar compositions of the untreated rocks, from 320.2 ± 10.0 Ma at 8 m from the niche MI to 333.3 ± 11.1 Ma at 1.97 m away (Table 4). An immediate conclusion is that these age data have no stratigraphic meaning, as the sequence is of Aalenian to Toarcian (183–170 Ma) stratigraphic age. They necessarily contain detrital minerals with K-Ar ages beyond the stratigraphic deposition reference. In the detail, the K_2O contents of the analyzed samples remain quite narrow from 3.06 to 2.59%. This variation is within the 1.5% analytical uncertainty of the K determinations due a plausible interference of a natural heterogeneity of the analyzed rock volumes and no significant impact on the measured K. The variation of the K-Ar age values tends also to decrease slightly when approaching the niche, between 8 and 4.4 m, and it increases again towards the value of the farthest sample when collected closer.

Table 4. The K-Ar data of the OPA whole-rocks before and after the heating experiment.

Sample IDs	Place/MI Niche (m)	K_2O (%)	Rad. ^{40}Ar (%)	Rad. ^{40}Ar (10^{-6} cc/g)	Age (Ma +/− 2σ)
Initial					
BHE-D5 0	8.00	3.06	73.86	34.57	320.2 (10.0)
BHE D5 5B	7.96–8.15	2.63	26.46	30.88	331.7 (11.0)
BHE D5 4B	7.50–7.66	2.81	22.08	31.13	314.5 (10.2)
BHE D5 3B	7.00–7.21	2.87	22.47	31.27	309.7 (9.9)
BHE D5 2B	4.36–4.50	2.92	18.12	30.01	293.5 (9.3)
BHE D5 1B	2.10–2.24	2.76	25.77	30.32	312.0 (10.2)
BHE D5 7B	1.97	2.59	48.85	30.58	333.3 (11.1)
after heating					
BHE D5-3	7.00–7.21	2.69	51.70	30.57	345.0 (11.6)
BHE-D5 8	5.50–5.60	2.84	57.73	35.13	347.9 (11.2)
BHE-D5 6	2.45–2.60	2.88	32.10	33.70	330.7 (10.6)
BHE D5-1	2.10–2.24	2.65	37.10	32.96	326.1 (11.1)

IDs stands for identities, m for meters, and rad. for radiogenic.

3.2. The Characteristics of the Heated Opalinus Clay Formation

The already described morphological changes of the pyrite crystals suggest a discrete but pervasive contamination during coring, probably amplified by a bacterial pollution. After the heating test, the contents of the major elements of the rocks duplicate quite systematically those of the samples analyzed along the 8-m long cores before heating (Table 1). Among the visible changes are the Si contents that decrease towards the heater, together with those of Fe and K, whereas those of Ca and the LOI increase, also towards the heater (Figure 4). Most elemental contents scatter more widely, together with the LOI values, along the lastly drilled BHE-D26 core. A few variations concerning specifically the alkali and alkali-earth elements were observed locally. For instance, the sample located 3.3 m from heater is enriched in Ca compared to the other samples, while the sample located at 0.27 m from heater is enriched in MgO and depleted in K_2O. Again, part of these variations most probably results from discrete lithological variations expected in the studied rocks, as was the case along the BHE-D5 core. When compared to the initial unheated rocks, the chemical compositions of the heated counterparts show no significant variations in the major elements. Except for Ca and Si, the changing contents could relate to lithological variations rather than to the heating impact. Also, no chemical trend correlates with the distance to the heater (Figure 4).

The elemental contents of the rocks leached with dilute (1 M) HCl before and after heating were expected to provide information relative to their location along the drilled cores. The specific interest for the analysis of such leachates is the fact that the removed elements do not only result from mineral alteration induced by the heating impact, but more probably from amounts of soluble minerals. While quite stable away from heater, the leached Si decreases markedly by a factor of 4 when approaching the heater, the same occurring for Al and K (Table 2). These changes obviously relate to a mineralogical change in the rock collected next to the heater and were apparently induced by it. The removed elements remain quite constant away from heater, except Ca that increased continuously towards the heater before the experiment. After heating, the leached Si, Al and Mg decrease slightly towards the heater as do Na and K, while Ca remains about constant (Figure 7). This progressive decreasing contents of the former of these elements when approaching the heater are, together with an increase before heating, in favor of a discrete mineral reorganization induced by the experiment. As the amounts of leached elements are systematically lower after heating, which implies a crystallization of new soluble minerals that incorporated only part of the elements freed by the heating episode. In the detail, most of these elements are probably constitutive of chlorides, carbonates and/or sulfates dissolved by local pore fluids diffusing in the rock matrix when the temperature increased. Some were most probably trapped again by newly crystallizing soluble minerals at the end of the experiment when the temperature declined again, while the remainder of the fluids could have been driven out of the controlled rock volume.

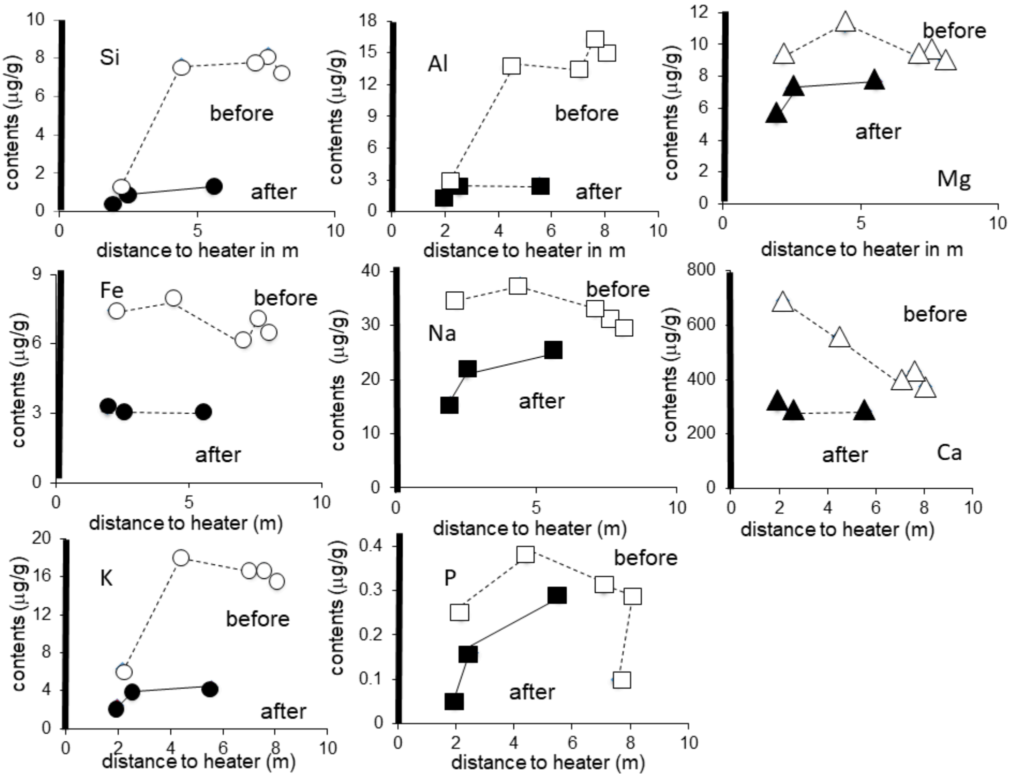


Figure 7. Variations of the elemental contents from OPA rock leachates of the OPA whole rocks before and after the heating experiment.

Before heating, the contents in REEs of the rocks collected along borehole D5 varied between 113.6 and 131.6 µg/g. They increase significantly after heating from 190.1 to 251.9 µg/g in the samples of bore hole D26 (Table 3). Therefore, the impact is easily visible by the REEs contents. On the other hand, the distribution of these REEs relative to the NASC reference is not changing significantly (Figure 6A,B). Indeed, after an incurved distribution for the LREEs La to Nd, the patterns decrease until Tb, have a short increase for Dy, decrease again until Tm and finally increase until Lu. This distribution remains similar for the heated rocks with a slight change for sample D26-8 that yields the same distribution but higher contents, and for sample D26-10 with higher Sm and Eu contents. In turn, heating impacted the contents of the rock REEs, but not really their distribution patterns. A preliminary assumption for the difference in the contents with very similar patterns could be the dissolution of homogeneous soluble minerals due to heating and fluid revival, with lower REE contents but similar distribution patterns than for the remaining insoluble counterparts.

The REE contents of the rock leachates are low and narrowly scattered along the borehole containing the heater (Table 5). Before heating, the amounts decrease from 17.9 µg/g close to the wall of the MI niche to 13.0 µg/g away from the wall. After heating, the amounts are slightly lower, between 14.7 µg/g away from heater to 12.7 µg/g next to it. However, the distribution patterns outline a decrease away from the gallery wall, even if the contents of the leached REE remain similar after heating. If resulting from an earlier excavation of the gallery, it would also explain the increase of P due to plausible atmospheric contamination. In turn, leaching with dilute acid removes constant amounts of REEs that remain about the same after heating, which suggests that the main REE carriers were apparently not altered. It also confirms that the REEs do not solubilize preferentially in diffusing fluids.

Table 5. The rare-earth elemental contents of the OPA whole-rock leachates by dilute acid before and after the heating experiment.

Sample IDs	Location/ Probe (m)	La (μg/g)	Ce (μg/g)	Pr (μg/g)	Nd (μg/g)	Sm (μg/g)	Eu (μg/g)	Gd (μg/g)	Tb (μg/g)	Dy (μg/g)	Ho (μg/g)	Er (μg/g)	Tm (μg/g)	Yb (μg/g)	Lu (μg/g)	Total (μg/g)
initial																
BHE-D5-8	5.50–5.60	1.21	1.25	1.26	1.24	1.25	1.28	1.32	1.28	1.30	1.28	1.28	1.27	1.35	1.28	17.85
BHE-D5-6	2.45–2.60	1.02	1.03	1.03	1.02	1.03	1.03	1.04	1.04	1.04	1.05	0.77	0.75	0.82	0.78	14.49
BHE-D5-7	1.90–2.00	0.95	0.94	0.92	0.92	0.91	0.89	0.91	0.89	0.90	0.91	0.91	0.97	0.97	0.94	12.93
after heating																
BHE D26-14	0.40	0.96	0.96	0.98	0.97	0.97	0.90	0.94	0.98	1.00	0.96	1.05	1.02	1.02	1.00	13.71
BHE D26-12	0.10	0.99	1.00	1.02	1.02	1.01	0.99	0.98	1.08	1.05	1.03	1.07	1.04	1.11	1.05	14.44
BHE D26-10	0.27	1.03	1.04	1.05	1.06	1.04	0.97	1.03	1.10	1.10	1.07	1.09	1.07	1.15	1.07	13.77
BHE D26-8	0.75	0.89	0.90	0.91	0.90	0.89	0.83	0.89	0.95	0.91	0.89	0.91	0.90	1.00	0.94	12.71
BHE D26-3	3.30	1.00	1.01	1.06	1.03	1.03	0.75	1.01	1.06	1.07	0.99	1.03	1.08	1.05	1.08	14.25
BHE D26-2	5.70	0.92	1.05	1.01	1.01	1.00	0.98	0.99	1.00	1.05	1.04	1.09	1.19	1.17	1.20	14.70

IDs stands for identities and m for meters.

The apparent K-Ar ages of the heated rocks measured after heating and storage are quite systematically higher than those of the samples taken before heating at about the same distance from the niche (Table 4). They range from 326.1 ± 11.1 Ma for the sample taken next to the niche to 347.9 ± 11.2 Ma for that collected 5.55 m away from the same niche. On the other hand, the K_2O contents between 2.65 and 2.88% are analytically similar to those of the rocks collected before heating. They are even identical to most of the unheated rocks except the higher 3.06% value of the unheated sample taken the farthest from the niche wall. As most data from heated rocks remain within the range of values obtained for the corresponding unheated samples, the small detected analytical scatter along the drilling profile appears to relate again mostly to slight mineralogical variations rather than to the impact of the experiment, as no clear systematic trend is observed as a function of the distance to the heater. In the detail, however, the comparison of the apparent K-Ar ages of the heated rocks with the initial references shows systematic slightly higher values after heating. This systematic increase of the K-Ar data ages is apparently related to an increase of the radiogenic ^{40}Ar, which was not really expected in the present conditions, as the K_2O contents are almost identical in the rocks before and after heating.

At this point, the changes in most elemental contents of the rocks and of their leachates after heating relate apparently more to discrete variations in the mineralogical compositions of the selected samples, rather than resulting from heating. The elements affected by heating, such as Ca, Na, Sr, the LOI and the REEs, could be constitutive of soluble minerals. On the other hand, the slight increase in radiogenic ^{40}Ar of the rocks is somehow unexpected, due to the "special" status of Ar that is not bound but squeezed within its host sheet minerals. It is considered to be most sensitive and, therefore, quite easily removable by any crystal modification (e.g., [31]).

3.3. The Results on the Boom Clay

The XRD data of the Boom rocks outline an irregular decrease of quartz until the second control after 1799 days of heating and a straight increase towards the end of the experiment. The feldspars remain at a constant amount during the whole experiment. The calcite and pyrite contents decrease slightly, as those of quartz until 1799 days, while increasing again towards the end of the experiment, the contents of dolomite and anatase remaining parochial during the whole experiment (Table 6). The contents of the 2:1 clay minerals tend to increase until the third control after 1799 days of heating and to decrease afterwards until those of the initial sample. The various clay components including illite, smectite, mixed-layers illite-smectite and smectite-chlorite, kaolinite and chlorite range also narrowly with a slight increase at the third control (Table 6). The mineral repartition of the initial reference rock and those subjected to 80 °C during 830, 1799 and 2529 days remains quite stable except for a decrease in quartz after 1799 days compensated by an increase of the 2:1 clay minerals. This mineral composition is typical for the undisturbed Boom Clay as reported earlier by Zeelmaekers et al. [19] and Frederickx et al. [20]. Mineral heterogeneity being excluded in this experiment, the observed variations resulted then, most probably, from heating. It may also be recalled that the controls had to remain limited because such batch experiment does not allow many stops and intermediate sample collections as each needs to open a container.

The decrease in the quartz content is confirmed by the variation of the SiO_2 values from 60.3% in the reference rock to about 54% after 2529 days of heating. Another significant change is the increase of Al_2O_3 from 16.1% to 19.8%, as well as that of MgO from 1.93% to 2.27%. On the other hand, K_2O increased moderately from 3.15% to 3.47%, while the other major elements remain more or less unchanged if considering the analytical uncertainty given above (Table 7, Figure 8). Also to be mentioned is a correlative increase of the same elements in the <2 μm fractions, except for P that decreases. Gentle leaching of the unheated rock and of that heated during 830 days focuses on a systematic increase of the leachate loads and, therefore, an overall elemental decrease in the rocks except for the increasing P content (Table 8). Also to be mentioned is a correlative increase of the same elements in the

<2 µm fractions, except again for P that decreases. Apparently, heating induced a transfer of major elements, probably volatile and/or soluble, from rock size into smaller crystals of the <2 µm fractions, unless smaller soluble minerals crystallized at the <2 µm size.

Table 6. The XRD mineral composition of the Boom Clay sample before and during the batch test.

Minerals	Initial Contents (%)	After 830 Days (%)	After 1799 Days (%)	After 2529 Days (%)
Quartz	23	16	12	23
Albite	7	6	6	6
K-feldspar	8	5	7	8
Calcite	4	2	1	3
Dolomite	0.6	0.7	0.0	0.1
Pyrite	4	2	2	3
Anatase	1	0.6	0.8	1
2:1 clay minerals	41	54	58	42
Smectite	12	14	15	12
Illite/Smectite	18	27	27	21
Illite	11	11	14	10
Kaolinite	4	5	2	2
KaoliniteSmectite	5	8	9	8
Chlorite	3	3	4	3

Table 7. Major elemental contents of the whole rock and <2 µm fraction of the Boom Clay during the batch test.

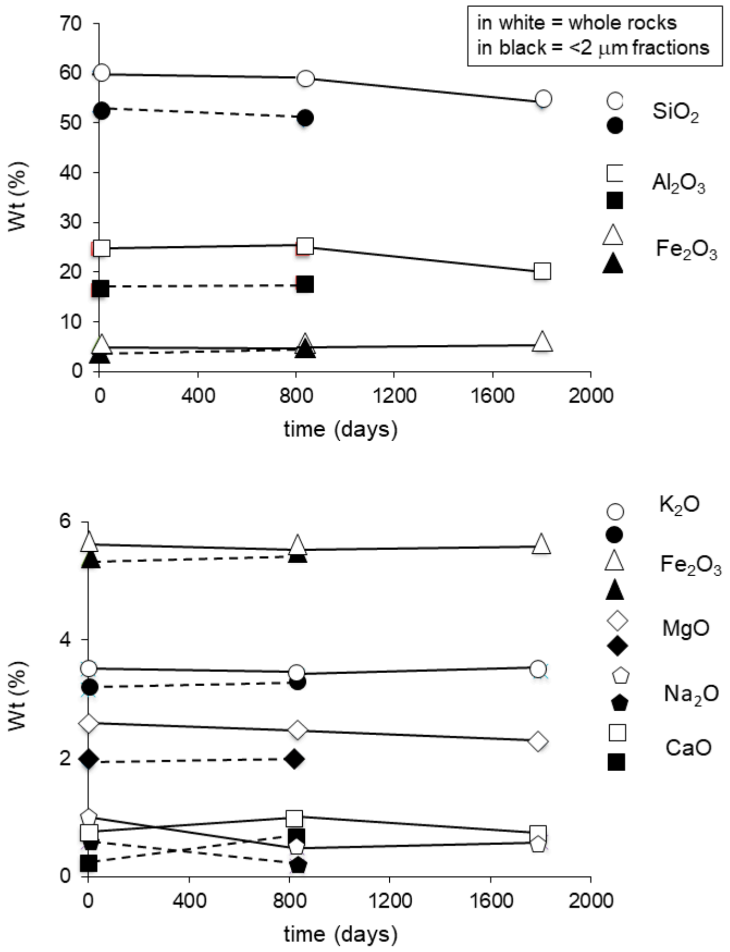
Sample Description	SiO_2 (%)	Al_2O_3 (%)	MgO (%)	CaO (%)	Fe_2O_3 (%)	Mn_3O_4 (%)	TiO_2 (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	LOI (%)	Total (%)
initial bulk	60.3	16.1	1.93	0.72	5.37	0.02	0.85	0.58	3.15	0.08	10.27	99.36
initial < 2 µm	52.2	24.4	2.55	0.21	5.64	0.02	0.84	0.93	3.51	0.10	9.56	99.96
Heat1 bulk (830 d)	58.9	17.6	2.00	0.65	5.53	0.02	1.04	0.49	3.38	0.11	10.33	100.09
Heat1 < 2 µm	50.5	24.5	2.45	0.94	5.50	0.02	0.76	0.17	3.40	0.07	10.79	99.15
Heat3 bulk (1799 d)	55.0	19.2	2.19	0.67	5.60	0.02	0.93	0.46	3.36	0.09	11.27	
Heat2 bulk (2529 d)	54.2	19.8	2.27	0.67	5.60	0.04	0.84	0.58	3.47	0.13	11.71	99.34

d stands for days.

Table 8. The major elemental contents of the dilute-acid leachates of the whole rock and <2 µm fraction powders of the Boom Clay during the batch test.

Sample Description	Si (µg/g)	Al (µg/g)	Mg (µg/g)	Ca (µg/g)	Fe (µg/g)	Mn (µg/g)	Ti (µg/g)	Na (µg/g)	K (µg/g)	P (µg/g)
initial bulk	2.2	1.44	9.64	36.4	2.69	0.07	0.04	27.1	13.1	2.30
initial < 2 µm	0.8	0.26	0.21	1.30	0.42	bdl	0.01	50.7	2.56	0.63
Heat1 bulk (830 d)	1.6	1.28	7.41	27.2	1.93	0.08	0.01	19.1	10.8	3.53
Heat1 < 2 µm	4.0	1.52	1.11	31.4	1.26	0.01	0.06	1.24	6.50	0.36

d stands for days.



Wt stands for weight

Figure 8. Variations of the major elements from Boom Clay whole rocks before and during the heating batch experiment.

The REE distribution patterns of the Boom Clay rocks yield, again before and after heating, similar patterns relative to the NASC reference, with noticeable Nd and Tb positive anomalies. However, if the patterns are very similar, the amounts of LREEs of the sample collected at the first control are significantly higher from La to Dy than those of the untreated rock (Table 9, Figure 9A). The patterns of the corresponding <2 µm size fraction remain also similar relative to the NASC reference, before and after heating, but with higher contents after heating (Figure 9B). Furthermore, the Nd and Tb anomalies disappear after heating, while that of Dy remains visible, as it was for the OPA material. A comparison of the REE distribution in the heated rock relative to the untreated reference shows a continuous decrease from La to Lu (Figure 9C), while the <2 µm fractions yield an incurved decreasing pattern from La to Dy and increasing from Dy to Lu (Figure 9D), still relative to the NASC reference. In summary, the REE distribution patterns of both the rock and the <2 µm fraction show systematic decreases of the heavier REEs after heating.

The K-Ar apparent ages of the unheated reference rock and of its <2 µm fraction are within analytical uncertainty with those of the same rock and <2 µm fraction after 830 and 2529 days of heating (Table 10). The K-Ar values of the rocks range from a starting 258.3 ± 7.3 Ma to 256.0 ± 13.3 Ma for that heated during 830 days and to 254.4 ± 8.0 Ma after 2529 days of heating. In the case of the size fractions, the K-Ar age data range from 223.5 ± 5.1 Ma for the untreated separate to 226.2 ± 7.1 Ma after 830 days of heating and to 240.3 ± 7.4 Ma for the last step. This last value is significantly higher than the two previous ones, but not outside the analytical uncertainty. Again, the values are far higher than the

Rupelian (34–28 Ma) stratigraphic age, confirming the occurrence of detrital minerals, even at the fine <2 μm size. Moreover, the constant K-Ar values for the rocks and for the size fractions before and after heating mean that the main K carriers muscovite and illite were not altered by the experiment.

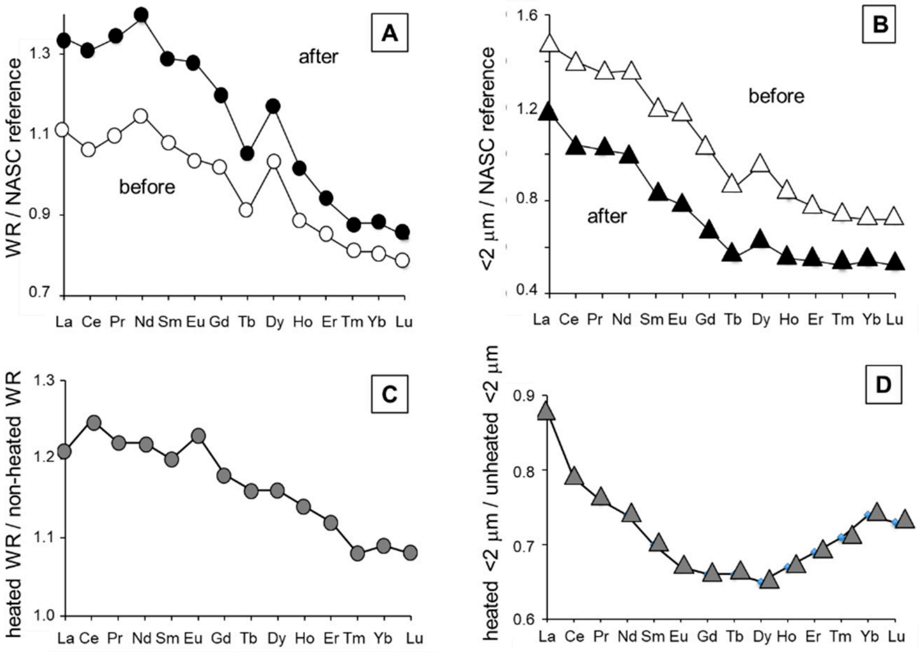


Figure 9. (**A**) REE distribution patterns of the Boom Clay rocks whole rock and (**B**) of the <2 μm fractions, before and after the heating batch experiment. (**C**) The REE contents of the heated whole rock were also compared to that of the initial contents, as well as those of the heated <2 μm relative to the initial fraction (**D**). WR stands for the whole rock heating experiment.

Table 9. The rare-earth elemental contents of the whole rock and <2 μm fraction of the Boom Clay during the batch test.

Sample Description	La (μg/g)	Ce (μg/g)	Pr (μg/g)	Nd (μg/g)	Sm (μg/g)	Eu (μg/g)	Gd (μg/g)	Tb (μg/g)	Dy (μg/g)	Ho (μg/g)	Er (μg/g)	Tm (μg/g)	Yb (μg/g)	Lu (μg/g)	Total (μg/g)
initial bulk	34.5	70.1	8.46	31.4	6.03	1.23	4.98	0.77	4.29	0.91	2.40	0.39	2.47	0.36	168.3
initial < 2 μm	45.7	93.2	10.4	37.2	6.70	1.38	5.01	0.73	4.00	0.84	2.19	0.35	2.21	0.33	210.2
Heat1 bulk (830 d)	41.6	87.7	10.3	38.2	7.23	1.51	5.88	0.89	4.89	1.04	2.68	0.42	2.68	0.39	205.4
Heat1 < 2 μm	36.7	69.3	7.86	27.5	4.66	0.92	3.30	0.48	2.59	0.56	1.52	0.25	1.64	0.24	157.5

d stands for days.

Table 10. The K-Ar data of the whole rock and <2 μm fraction of the Boom Clay during the batch test.

Sample Description	K (%)	rad ^{40}Ar (10^{-9} mol/g)	^{40}Ar (%)	Age (±2σ) Ma
initial bulk	2.62	1.26	37.82	258.3 (7.3)
initial < 2 μm	2.91	1.20	82.80	223.5 (5.1)
Heat1 bulk (830 d)	2.81	1.34	15.65	256.0 13.3)
Heat1 < 2 μm	2.82	1.18	26.32	226.2 (7.1)
Heat2 bulk (2529 d)	2.74	1.30	27.56	254.4 (8.0)
Heat2 < 2 μm	2.84	1.27	30.22	240.3 (7.4)

4. Discussion

The available analyses allow discussing the chemical and isotopic, and therefore the mineralogical changes of two sedimentary formations subjected to continuous low-thermal imprints along two independent experiments. As the generated temperature increase concerns more specifically the first meter around the heater in the case of the in situ experiment, samples located in this rock volume were more detailed in the comparisons. At this point, the three OPA samples (BHE-D5-3, D5-4, D5-5) located far from the wall and the EDZ/EdZ zones of the MI niche and close to the heater are quite homogeneous in their mineral and chemical compositions.

4.1. The Changes in the Opalinus Clay

The OPA samples located away from heating devices and from EDZ/EdZ zones yield chemical and isotopic data that are slightly away from those of the samples taken closer to the heaters. These variations concern more specifically the signatures of soluble phases as their contents decrease when approaching the MI niche [2]. Apparently related to oxidizing processes due to earlier excavations of the gallery and the niche, they could be due to the longer exposition of the rocks to the atmosphere, rather than to the strict heating experiment, which agrees with the above shown SEM pictures. Very limited, they appear as representative for the 4 to 5 m wall rocks of the niche and, therefore, confirm a more pervasive impact due an earlier dehydration.

The mineralogical, chemical and isotopic data of the heated OPA samples do not outline significant changes beyond analytical uncertainty. The homogeneous K-Ar data of the samples collected far from and next to the thermal probe confirm this observation. The temperature applied to the sediments, which is considered to be representative of the potential heat produced by stored nuclear waste, did not trigger significant chemical and Ar isotopic changes. As the formation already underwent a natural burial-induced diagenetic episode during its earlier evolution with a temperature reaching at least 85 °C [32], one may expect that most or at least part of the changes occurred during this earlier natural diagenesis, especially with an impact during millions of years and not during months like for the experiment. The artificial heating did obviously not generate new altering reactions, which focuses on the maturity of the clay formation in its long-term behavior relative to any moderate thermal imprint like applied here. For a geological disposal of exothermic radioactive waste, this aspect is of importance, as the characteristics of the host formation need to be maintained during a longer period by the waste itself in a mature clay-type host sedimentary sequence, such as the OPA formation.

However, a discrete chemical evolution cannot be denied when comparing the initial and the post-heating releases into the OPA leachates, that is to say those released by the soluble minerals. Basically, the observed changes relate to elements either adsorbed on mineral surfaces or released from soluble minerals sensitive to slight temperature modifications. Such changes are asserted here by: (1) a destabilization of pyrite with a visible alteration of the crystals and the formation of blurry veils around them, probably favored by a bacterial contribution during drilling or since, and (2) a slight increase of the rock K-Ar age values. This latter change was somehow unexpected because it usually occurs only when either the K_2O content decreases and/or when that of the radiogenic ^{40}Ar increases. Here it outlines fresh information as the K_2O data of the rock samples did not change due to the heating experiment, the only explanation being then a higher content of radiogenic ^{40}Ar in some kind of mineral structures relative to the atmospheric ^{40}Ar (Table 5). The differential behavior of an inert gas, such as Ar, can only occur if the radiogenic ^{40}Ar issued from decay of the ^{40}K is retained differently than the atmospheric ^{40}Ar in the K-rich sheet-silicate minerals, such as the micas and their micrometric illite-type minerals. An immediate interpretation would then be in an increase in the radiogenic ^{40}Ar content during a degasing action, as was the case for the OPA rocks. Such behavior is analytically realistic as a preferential "degassing" of the atmospheric ^{40}Ar without any other noticeable impact on the occurring minerals, including the labile K-carrier clay minerals.

4.2. The Changes in the Boom Clay

The heated Boom Clays do, also, not outline significant mineralogical, chemical and K-Ar isotopic changes after 2529 days of heating at 80 °C. All identified mineral phases are still present in the heated samples, although with slight changes in their amounts, as suggested by the quantitative XRD and wet-chemistry analyses. In contrast, the comparison of the leachates from non-heated rock and <2 µm fraction with those from heated equivalents focuses on following changes: the contents of all major elements decrease slightly in the rocks, except that of increasing P, while the contents of the same elements from <2 µm fractions increase except, again, that of decreasing P.

The K-Ar data of the untreated rock and <2 µm fraction are strictly within those of the same rock and <2 µm separate after 830 and 2529 days of heating (Table 9). The number of analyzed samples and fractions being limited for reasons explained above, the discussion about the meaning of the K-Ar data is somehow tied. However, by comparing the data of the initial <2 µm fraction and that after 2529 days of heating, the latter yields a significantly higher K-Ar age data than the untreated reference and than that after 830 days. In fact the increase from 223.5 ± 5.1 to 240.3 ± 7.4 Ma is not due to a changing K content and has, then, to result from an "increase" of the radioactive ^{40}Ar, as was already observed for the OPA material.

The slight changes in the major elemental contents of both the rocks and the <2 µm fractions suggest some transfers of soluble elements from bulk to the <2 µm fractions. A determining aspect is provided, again, by the K-Ar data with an increase of the K content from rocks to their <2 µm fractions, which is related to the increasing amount of K-carriers in the size fractions relative to the whole rocks that contain also coarser crystals of detrital origin, such as quartz and the feldspar grains for instance. This increase is systematically accompanied by a slight decrease in the radiogenic ^{40}Ar content, both resulting in a decrease of the K-Ar age date. In turn, the probable elemental transfers from rocks to the <2 µm fractions seems not to affect the K-Ar data, except the unexpected increase of radiogenic ^{40}Ar. In turn, the K-Ar data suggest also that none of the K carriers of the rocks and the <2 µm fractions were altered by the temperature applied during the 7 years.

4.3. To Which Extent Did the Artificial Temperature Impact the Studied Material?

The data of the Boom Clay experiment build an interesting analytical basis to formulate a transfer of volatile and soluble elements from coarse to fine sized minerals, unless the coarser sized minerals lost more volatile and soluble material than the minerals of smaller size. The K-Ar data of the bulk and <2 µm fractions consolidate also the fact that all K carriers, whatever their size, remained inert during the heat experiment.

The in situ heating of the OPA sediments is close to real deep-storage conditions with the heater working at about 100 °C during 8 months and a final sampling along transversal drillings. The weak aspect is the fact that the controls after heating needed supplementary drillings that, even located very closely to the initial samples, gave samples with mineral compositions plausibly yielding mineral heterogeneity, even very limited, of the sedimentary sequence. It cannot, therefore, be excluded that this mineral heterogeneity could have introduced some minor and uncontrolled biases in the necessary comparisons. In fact, only Ca, Na, Sr, the LOI and the REEs seem to have been affected by the long-term heating with a few variations beyond analytical uncertainty. Most of these elements are major constitutive components of soluble minerals such as the carbonates or the chlorides, a relation supported in turn by the LOI trend.

The data collected during the Boom Clay experiment build an interesting analytical basis to formulate a transfer of volatile and soluble elements from coarse to fine sized minerals, unless the coarser minerals lost more volatile and soluble material than those of the <2 µm separates. The K-Ar data of the bulk and <2 µm fractions consolidate also the fact that all K carriers, whatever their size, remained inert during the heat experiment.

In fact, the most unexpected results are provided by the K-Ar data with a heating-induced increase of the radiogenic ^{40}Ar that basically results from disaggregation of the radioactive ^{40}K. Visible in both studied sequences, this increase is necessarily meaningful, as each studied sequence yields different lithologies, as well as different stratigraphic and isotopic ages. The fact that the results are similar in both sequences heated during two independent experiments constitutes a solid basis for the observation. Heating moderately sediments in their natural environment, as well as in batches, is expected to impact at least, the adsorbed gaseous content of some of the constitutive minerals. In fact, the K-Ar data suggest that the atmospheric ^{40}Ar is basically more affected by a temperature increase than the radiogenic ^{40}Ar, the former being expected to decrease and the latter to increase relatively. It is then plausible that the two Ar isotopes that are of different origins are stored at different places of the host sheet-silicates such as the micas and the micrometric argillaceous illite and illite-smectite mixed-layers. To the best of our knowledge, this is the first time such a differential behavior among Ar isotopes is observed and reported. The earlier excavations of the galleries and niches could have added fluctuations on top of those known for the Ar isotopes that are only secured in crystals by van der Waals bonding. On the other hand, these K-Ar results point towards a specific aspect of the method due to the easy escape of any of the Ar isotopes. Here, the radiogenic ^{40}Ar is surprisingly less easily removed than its atmospheric equivalent by a low heating during several months to years as its content tends to increase. Such increase only can result from a more efficient retention in the mineral structure than the other trapped gases including the atmospheric Ar. An alternative behavior could be due to atmospheric ^{40}Ar only adsorbed on the crystals, while radiogenic ^{40}Ar would be more secured in the crystals because resulting from ^{40}K disintegration.

In summary, the low heat applied to the two sedimentary sequences along two independent experiments has apparently only a very limited impact that induced: (1) a dissolution of soluble minerals, such as carbonates, sulfates and chlorides, due to the mobilization of a limited amount of fluids in the rocks, and (2) some degassing of elements rather adsorbed on than trapped in mineral structures.

5. Conclusions

Two independent heating experiments, one in situ and one in batch containers, were applied to cores samples from Aalenian-Toarcian Opalinus Clay in the Swiss Jura (Switzerland) and from Rupelian Boom Clay ground-material heated during 7 years at Mol (Belgium). These experiments were designed and completed to test the impact of 80–100 °C temperature rises on sediments currently studied as potential deep host repositories for nuclear waste, as such temperature increase is theoretically expected by stored nuclear waste on the host rocks at the disposal sites.

The Opalinus Clay rocks were heated by devices inserted into drillings during 8 months and set at about 100 °C. Some natural mineralogical heterogeneity of the rocks was an identified drawback of the design that could not be ignored. It had to be taken into account with, consequently, limited uncontrolled dispersions in some of the elemental and isotopic data. Despite this sampling aspect, the contents of most major, trace and REEs remained within analytical uncertainty, except Ca, Na, Sr and the REEs which contents, as well as the loss on ignition were affected beyond the analytical uncertainties. The results of the solid rocks match well with a systematic low removal of the same elements from heated samples after leaching with dilute hydrochloric acid. Globally, the observed releases suggest a predominant alteration of carbonates, chlorides and/or sulfates. The drawback of the batch experiment on the Boom Clay is in the necessarily limited control stops because each needs the opening of a container. Despite this aspect, the batch experiment complements well the data of the in situ experiment on the Opalinus Clay by only limited elemental transfers of only soluble minerals, the coarser minerals releasing possibly more elements than the finer. It also cannot to be excluded that some tiny minerals crystallized again in the fine fractions. In fact, no element yields changes that are clearly beyond analytical uncertainty, with the conclusion that the heat did not alter the major constitutive minerals.

The K-Ar data of the two heated rock formations provided unexpected increases of radiogenic ^{40}Ar relative to atmospheric ^{40}Ar. They suggest, in two independent experiments on two different sedimentary formations, that the latter of these isotopes is more easily removed by heating than the former. The two Ar isotopes apparently are hold differently in the K-bearing mineral space, especially of micas and argillaceous illite and illite-smectite mixed-layers, with results in favor of a preferential release of atmospheric ^{40}Ar relative to radiogenic ^{40}Ar by heating. A spontaneous interpretation is in a different holding/setting than for the other gases, the atmospheric ^{40}Ar being only adsorbed to crystals while the corresponding radiogenic ^{40}Ar is better secured in the crystals. Therefore, this differential behavior might become an interesting test for the evaluation of the potential sealing characteristics of potential host sediments.

Importantly, the different analytical protocols tested here on two sedimentary formations point to identical conclusions, namely that an extended 80–100 °C temperature increase does not alter the sealing characteristics of the studied formations. In other words, the impact by spontaneous heating does not alter the safety-related properties of the studied potential host sediments.

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