



Structural modifications of Callovo-Oxfordian argillite under hydration/dehydration conditions

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Abstract

The clay minerals are among the first silicated minerals to be transformed physically and chemically during changes of temperature, pressure, relative humidity and fluid composition. One of the first physical processes, extremely rapid, is the hydration and/or dehydration of swelling clays minerals. These processes could generate changes of the clay structure and consequently the texture of an argillaceous rock. In order to observe in situ structural modifications on a deep argillaceous rock “argillite” (Parisian basin, in France) according hydration–dehydration cycles, an Environmental Scanning Electron Microscope (ESEM) was used. This instrument allows the possibility to observe geological samples in their natural state without preliminary preparation or modification. Two types of samples were prepared, parallel and perpendicular to the lithology. Then, each sample was submitted to three water condensation/evaporation cycles.

The observed samples were from the Callovo-Oxfordian formations in HTM 80743, HTM 983, HTM 02618 and EST 2159 cores. ESEM observations show that the water sensitivity of these bulk samples depends directly on the clay mineral proportion in the rock, and on the clay family present. It is also obvious that the water sensitivity depends on the anisotropy of the pore structure and the particle size and total porosity. The main structural modifications observed were the cracking of the surface, particles aggregation/disaggregating and opening/closing of pores and/or cracks.

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1. Introduction

The Environmental Scanning Electron Microscope (ESEM) was introduced in the last decade. It differs from the conventional Scanning Electron Microscope

on the permitted presence of a low vacuum in the sample chamber. Thus, wet, oily, dirty, or non-conductive samples can be examined in their natural state without modification or preparation (Jenkins and Donald, 2000). The sample environment can be varied through a range of pressures or temperatures (Baker et al., 1995).

The sample temperature ranging from – 5 up to 55 °C is controlled by a “cooling stage” installed on the

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Table 1
Mineral composition of Callovo-Oxfordian argillites (ANDRA, 1996)

Identification			Mineral composition (wt.%)			
Sample	Drilling	Depth (m)	Clays	Carbonates	Quartz	Others
HTM 02618	HTM102	363	13	40	36	11
HTM 983	HTM102	399	50	21	22	7
HTM 80743	HTM102	466	55	16	21	8
EST 2159	EST104	447	26	23	40	11

Semi-quantitative analysis of X-ray diffraction.

ESEM. A differential pumping system enables also the control of the ESEM chamber pressure ranging from 0.1 up to 10 Torr. These combined factors make the ESEM a powerful tool for investigating the in-situ interactions between clay minerals and water (Baker et al., 1995; Rodriguez-Navarro, 1998). In this paper, the main interest was effectively to study the interactions between the argillaceous rocks and water.

One of nuclear waste disposal concepts proposes to store waste in deep impervious clay geological layers. Vitrified waste is laid in canisters in the middle of a gallery dug in the clay formations. In France, the Callovo-Oxfordian formations (Parisian basin) were chosen to study this possibility of deep storage. The national agency of the radioactive wastes management (ANDRA) constructed an experimental underground laboratory within the Callovo-Oxfordian formations. The mineral composition in these formations varies as a function of depth. For example, in the first 40 m, the dominant minerals are quartz and carbonates (about 35% and 40%, respectively), and the clay proportion is of about 15%. In contrast, after 40 m, the Callovo-Oxfordian stratum presents a dominant clay proportion (about 40%). The proportion of accessory minerals remains constant in the Callovo-Oxfordian stratum (Rousset, 2002; Rousset et al., 2001). This heterogeneity on the mineral composition also allows to imagine a heterogeneous physico-chemical alteration because the presence of numerous physico-chemical process in the nuclear waste disposal systems. For example, the temperature increment during the disintegration reactions of wastes and different transport phenomenon could produce the instantaneous dry/wet cycles into the system. Then the clay minerals could be the first silicate minerals which are transformed during the dry/wet cycles. Several mechanical methods have

shown that the mechanical resistance of the Callovo-Oxfordian argillites decreases when they are previously immersed in water (Bauer-Plaindoux et al., 1997), because of high water sensitivity of this argillaceous rock. The previous observations justify the importance to observe in situ the structural modifications of Callovo-Oxfordian argillites. An Environmental Scanning Electron Microscope coupled with a cooling stage to control the sample temperature has been used. The control parameters were the lithology (side parallel and side perpendicular of the samples) and the water condensation/evaporation cycles (Montes, 2002). Four samples with different mineral compositions were studied (labelled HTM 80743, HTM 983, HTM 02618 and EST 2159) to estimate the influence of clay proportion and clay family in the rocks.

2. Material and methods

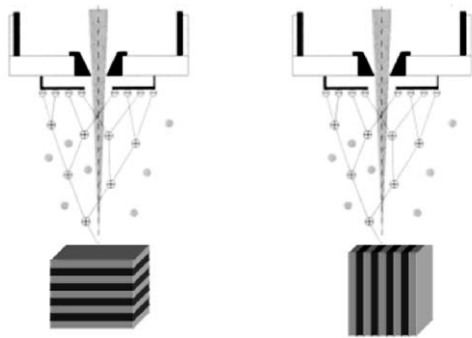
2.1. Mineral composition

The mineral composition of the Callovo-Oxfordian argillites varies as a function of the depth (ANDRA, 1996). In addition, the mineralogical analyses of the clay fraction (<2 μm) show a mineralogical change after 410 m depth by disappearance of illite/smectite interstratified clay minerals and sometimes the appearance of kaolinite. Tables 1 and 2 present the mineral composition and depth of the samples. The values presented in Tables 1 and 2 were estimated by semi-quantitative analysis of X-ray diffraction (ANDRA, 1996). Recently, these values were verified also using the semi-quantitative analysis (Rousset, 2002).

Table 2
Mineralogical analyses on the clay fraction (particles <2 μm) of Callovo-Oxfordian argillites

Identification			Clay composition (wt.%) (particles <2 μm)			
Sample	Drilling	Depth (m)	Illite	Illite/ smectite	Kaolinite	Chlorite
HTM 02618	HTM102	363	22	70	–	8
HTM 983	HTM102	399	25	65	–	10
HTM 80743	HTM102	466	40	12	35	13
EST 2159	EST104	447	15	85	–	–

Semi-quantitative analysis of X-ray diffraction.



Side-parallel to the lithology Side-perpendicular to the lithology

Fig. 1. Samples orientation in the ESEM chamber.

2.2. Observation conditions

For all environmental scanning electron microscope investigations, a XL30 ESEM LaB6 (FEI and Philips), fitted with a gaseous secondary electron

detector (GSED) to produce a surface image was used. This microscope is also equipped with a “cooling stage” to control the sample temperature.

Two types of samples were prepared, (a) side parallel and (b) perpendicular to the lithology (see Fig. 1). The samples were then separately submitted to three water condensation/evaporation cycles. Each cycle comprises three stages:

- (1) Drying. The chamber pressure and sample temperature are respectively fixed at 2.3 Torr and 50 °C. In this case, the relative humidity of the sample is 2.5% according to the water phase’s diagram. The sample is maintained at these “reference conditions” for about 20 min, and an image of interest is chosen and stored in the hard disk of the control PC.
- (2) Water condensation. The chamber pressure and the sample temperature are simultaneously set at 8.6 Torr and 8 °C, respectively. In general, this stage takes approximately 30 min.

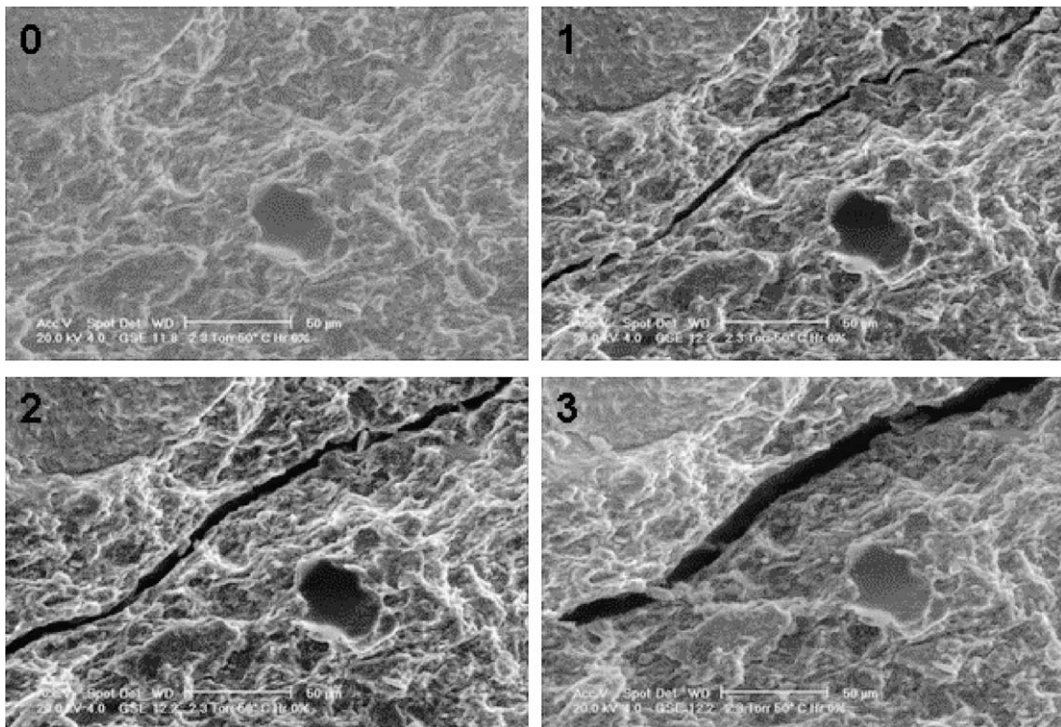


Fig. 2. Progressive cracking as a function of water condensation/evaporation cycles in the ESEM. Side-perpendicular to the lithology “HTM 80743 sample, sampling depth = 466 m”. (0) Initial conditions; (1) first cycle; (2) second cycle; (3) third cycle.

- (3) Water evaporation. Here the chamber pressure and sample temperature are again brought back at reference conditions ($P=2.3$ Torr and $T=50$ °C). After 20 min, the image of interest was stored again.

In order to not modify the original clay structure/texture of the samples before performing the ESEM study, each sample was prepared some minutes before ESEM observation. The procedure was very simple. First the argillaceous rock was oriented vertical or horizontal to the lithology, then the argillaceous rock was carefully taped to obtain the representative cuts where the dimensions were similar for all preparations ($4 \times 4 \times 2$ mm). Finally, the fine particles adhered at the surface, were removed by nitrogen gas.

3. Results and discussion

The water sensitivity of Callovo-Oxfordian argillites depends highly on the mineral composition (Figs.

2, 3, 4 and 5) and increases when the clay proportion increases. These results are compatible with the results obtained by mechanical methods (Bauer-Plaindoux et al., 1997).

The sample side-perpendicular to the lithology is more water sensitive than the sample side-parallel because the porosity is directly accessible to the water (Fig. 6). The sample side-perpendicular also enables to observe the swelling of the clays (Fig. 7). It is evident that sample side-parallel is less water sensitive, however, an aggregation/desegregation of small particles was observed at high magnification (Fig. 8).

A high water sensitivity of Callovo-Oxfordian argillites implicates the cracking, the aggregation/desegregation of small particles and a closing/opening of pores and/or cracks. Fig. 2 (sample HTM 80743) shows clearly a progressive cracking when the number of water condensation/evaporation cycles increases. In contrast, a non-progressive cracking was observed in Fig. 3 (HTM 983). In this case, there was cracking visible after the first cycle but after the second and

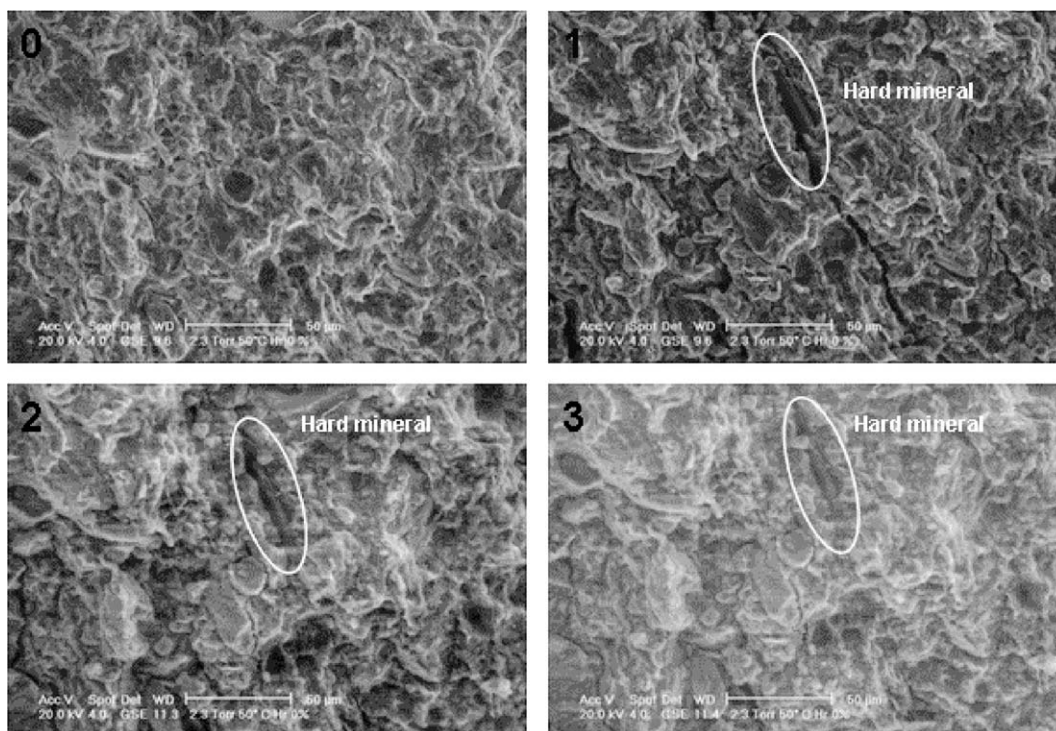


Fig. 3. Complex cracking (partial closing of the cracks) as a function of water condensation/evaporation cycles in the ESEM. Side-perpendicular to the lithology “HTM 983 sample, sampling depth = 399 m”. (0) Initial conditions; (1) first cycle; (2) second cycle; (3) third cycle.

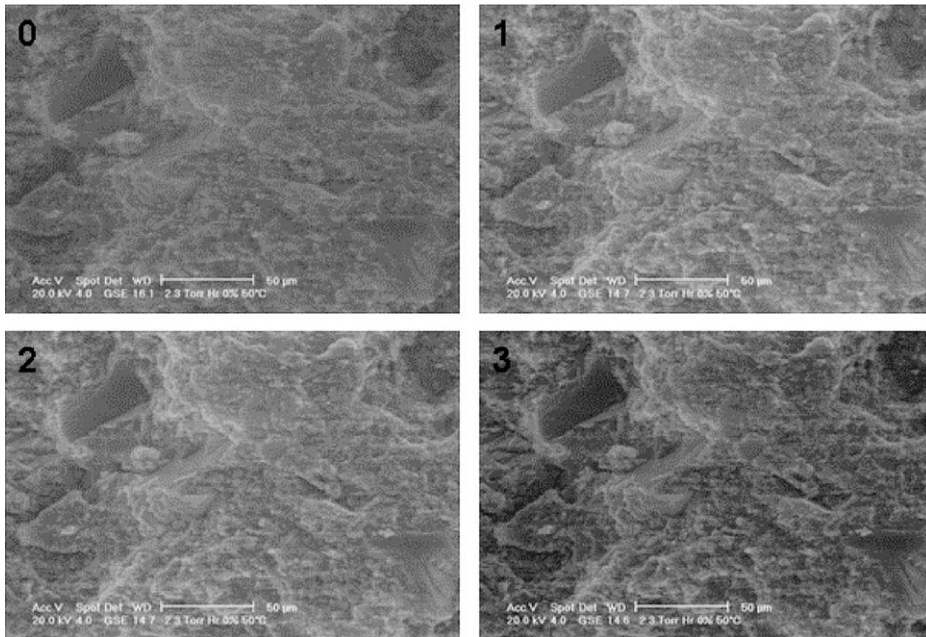


Fig. 4. Non-sensitivity to the water condensation/evaporation cycles. Side-perpendicular to the lithology “HTM 02618 sample, sampling depth=363 m”. (0) Initial conditions; (1) first cycle; (2) second cycle; (3) third cycle.

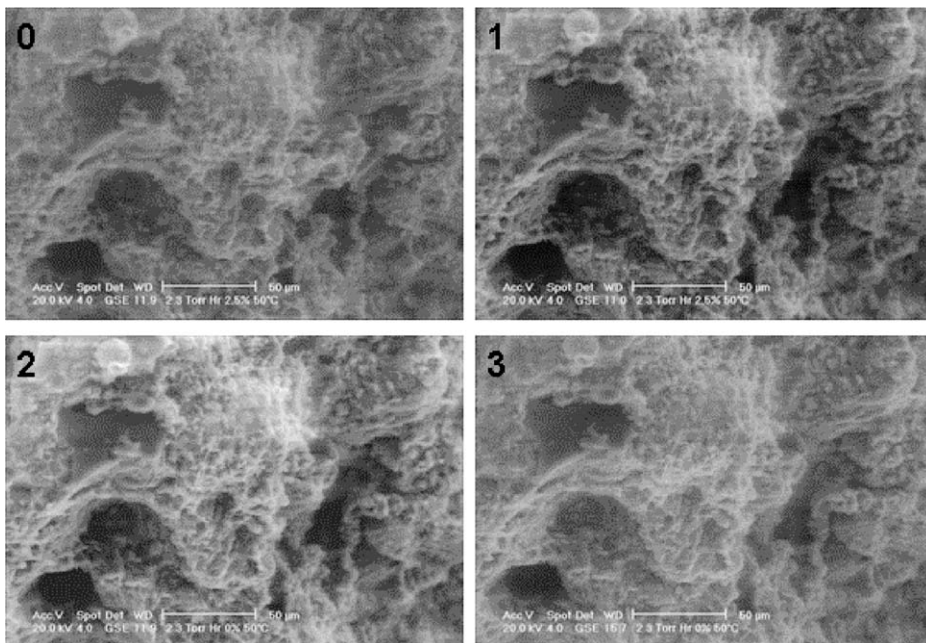


Fig. 5. Non-sensitivity to the water condensation/evaporation cycles. Side-perpendicular to the lithology “EST 2159 sample, sampling depth=447 m”. (0) Initial conditions; (1) first cycle; (2) second cycle; (3) third cycle.

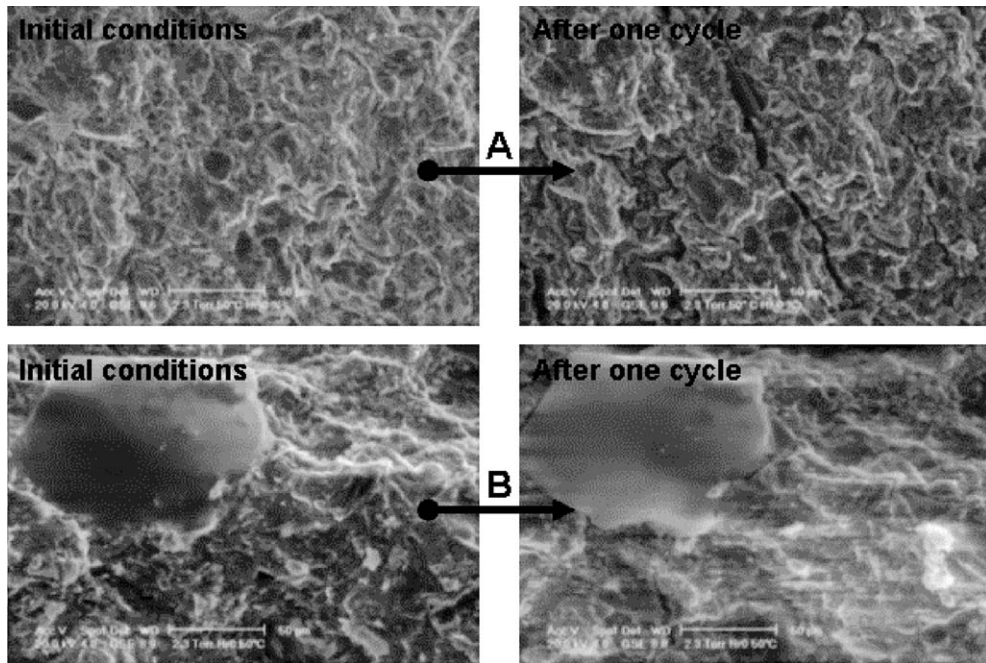


Fig. 6. Comparison of the water sensitivity after one water condensation/evaporation cycle “HTM 983 sample, sampling depth = 399 m”. (A) Side-perpendicular to the lithology; (B) side-parallel to the lithology.

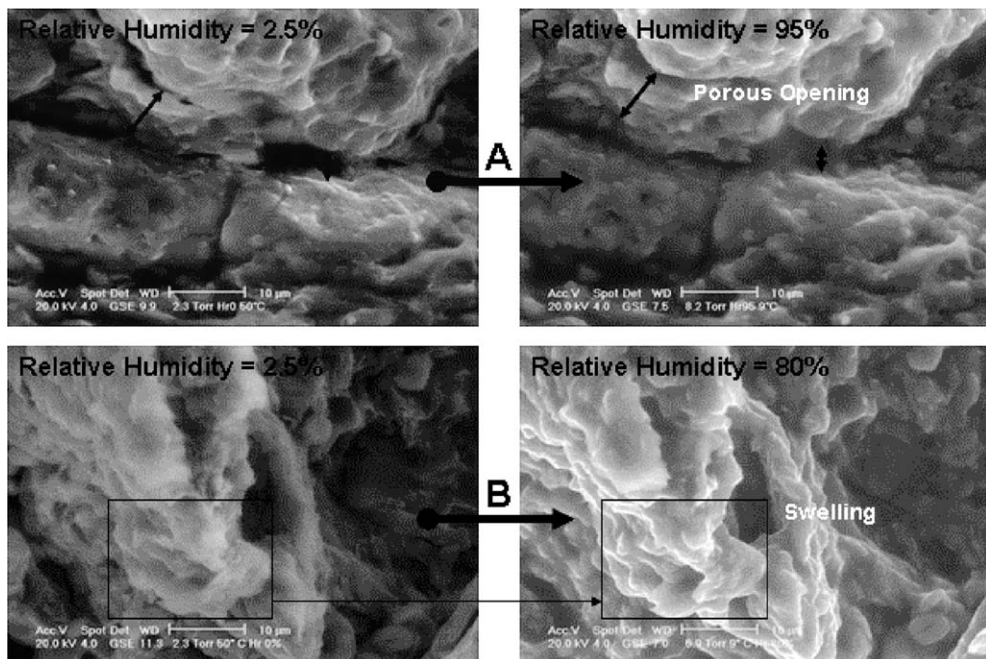


Fig. 7. Pore opening and swelling under wetting conditions “HTM 983 sample, sampling depth = 399 m”. (A) Side-parallel and (B) Side-perpendicular to the lithology.

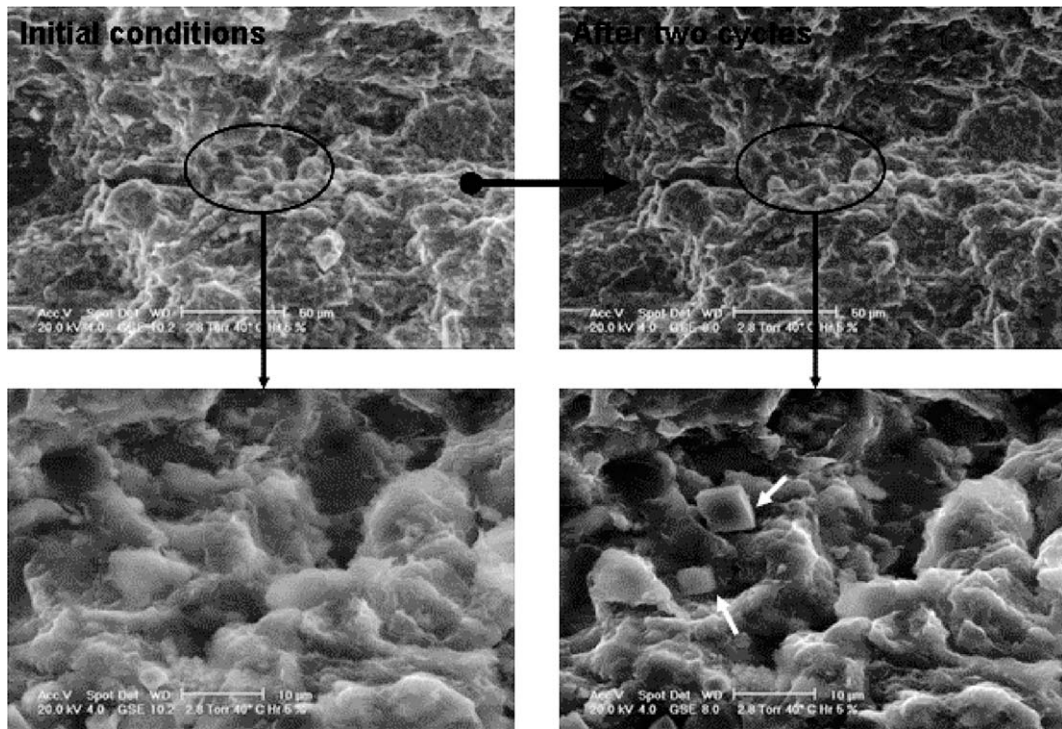


Fig. 8. Aggregation/desegregation of small particles “HTM 80743 sample, sampling depth = 466 m”. Side-parallel to the lithology.

third cycles a partial closing of cracks was observed. The cracking behaviour depends exclusively on the dominant clay family present in the rock, i.e. a progressive cracking is characteristic for rocks with dominant non-swelling clays while complex cracking (opening/closing of cracks and/or pores) is characteristic for rocks with dominant swelling clays.

The presence of non-deformable minerals of high size could favour the cracking (Fig. 3).

For HTM 02618 and EST 2159 samples, a very low sensitivity to the water condensation/evaporation cycles was observed (Figs. 4 and 5) because of the presence of a large amount of non-swelling phases such as carbonates and quartz.

4. Conclusion

ESEM observations of the samples from the Callovo-Oxfordian formations in HTM 80743, HTM 983, HTM 02618 and EST 2159 cores show that the water sensitivity depends directly on the clay mineral pro-

portion and on the dominant clay family in the rock. Water sensitivity is more significant when the clay proportion increases. The progressive cracking, complex cracking and particle aggregation/desegregation indicate a high water sensitivity of an argillaceous rock. In fact, the cracking type was linked to the dominant family clay in the rock, i.e. a progressive cracking is characteristic for non-swelling clays (ex. Kaolinite) and complex cracking (opening/closing of cracks and/or pores) for swelling clays (ex. Illite/smectite interstratified). It is obvious that the water sensitivity also depends on the pore structure anisotropy, particle size and total porosity. These parameters were not considered in this qualitative study.

Acknowledgements

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