ESRF	**Experiment title:** X-ray micro-diffraction study of cement/claystone interfaces	**Experiment number**: 01-02-1008
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Introduction

An international research programme was launched at the Mont Terri Rock Laboratory (St-Ursanne, Switzerland) with the aim of improving current understanding of the interaction of cement with Opalinus Clay (OPA) (Mont Terri Project "Cement-Opalinus Clay Interaction (CI)" called "CI-project"). In a long-term field experiment, different kinds of concretes and bentonite were cast into two vertical boreholes in the OPA with a depth of ~6m. After two and five years of reaction, samples were retrieved by overcoring of the interface. From these samples thin sections of the cement/OPA interface were prepared. The thin sections were polished down to a thickness of ~20 µm and mounted on a 0.5 mm thick quartz glass support.

Experiment

The beam spot size available at beamline BM01A/SNBL (ESRF) was about 100x100 μm^2, the refined beam energy was 17.792 keV, corresponding to a wavelength of 0.6969 Å. A PILATUS 2M area detector from Dectris was used for recording intensities. Calibration of detector distances was done using the LaB6 standard. Measurements were carried out on selected points of interest (POI) in 100 µm steps across the interface between cement and OPA (Fig. 1a). Exposure time was varied between 2 and 5 min. Thin sections were mounted on a sample stage with a motorized rotational axis parallel to the motorized *z*-motion axis and perpendicular to the X-ray beam. They were oriented in a way that the cement/claystone interface line was normal to the rotational and *z*-axis, thus by movement along z, a series of rotational scans could be measured on a profile line across the interface zone. Samples were rotated on the POIs in angles of 40 ° collecting 1 image or in 0.5 steps colleting 100 images (50 °).

Data treatment was done using the SNBL software. After generating the composite image in axes of 2θ and azimutal angles it was transformed into a one-dimensional plot using the FIT2D software. Identification of the relevant phases was performed by a search in databases. Relative intensities along the transient were determined for selected mineral using characteristic 2θ positions of these minerals (Brownmillerite: 5.46°, 0 2 0; Calcite: 13.193° 0 1 4; Dolomite: 13.853°, 0 1 4; Illite: 8.964° 1 1 0; Kaolinite: 5.585°, 0 0 2; Muscovite: 10.683°, 0 2 3; Periclase: 19.032°, 2 0 0; Quartz: 9.39°, 1 0 0; Vaterite: 12.143°, 1 0 1).

Results

Fig. 1 shows the image of a thin section along with the XRD results. The reactive zone at the interface extends over about 600 µm into the cement. In this zone mineral degradation and neoformation occured. The resulting composition of the phase assemblage is different from that of non-degraded cement, and, of course, very different from the composition of OPA (Fig. 1b). Brownmillerite (ferrite) and periclase seem to be the only characteristic cement phases that persist in the degradation zone at the interface. Other cement phases usually readily detected in cement pastes by XRD, such as portlandite or ettringite, are completely absent in the reactive zone, indicating that these minerals had been dissolved after ingress of OPA porewater into the cement paste. Degradation of the cement paste increases towards the interface which is indicated by decreasing amounts of brownmillerite and periclase (Fig. 1b). Kaolinite and illite are typical clay minerals and there content increases in the clay (left side in Fig. 1b). Calcite, vaterite and dolomite are the carbonate minerals identified. There content increases in the reactive zone towards the clay boundary, indicating neoformation as a consequence of the ingress of carbonate rich OPA porewater into the Ca rich cement zone.

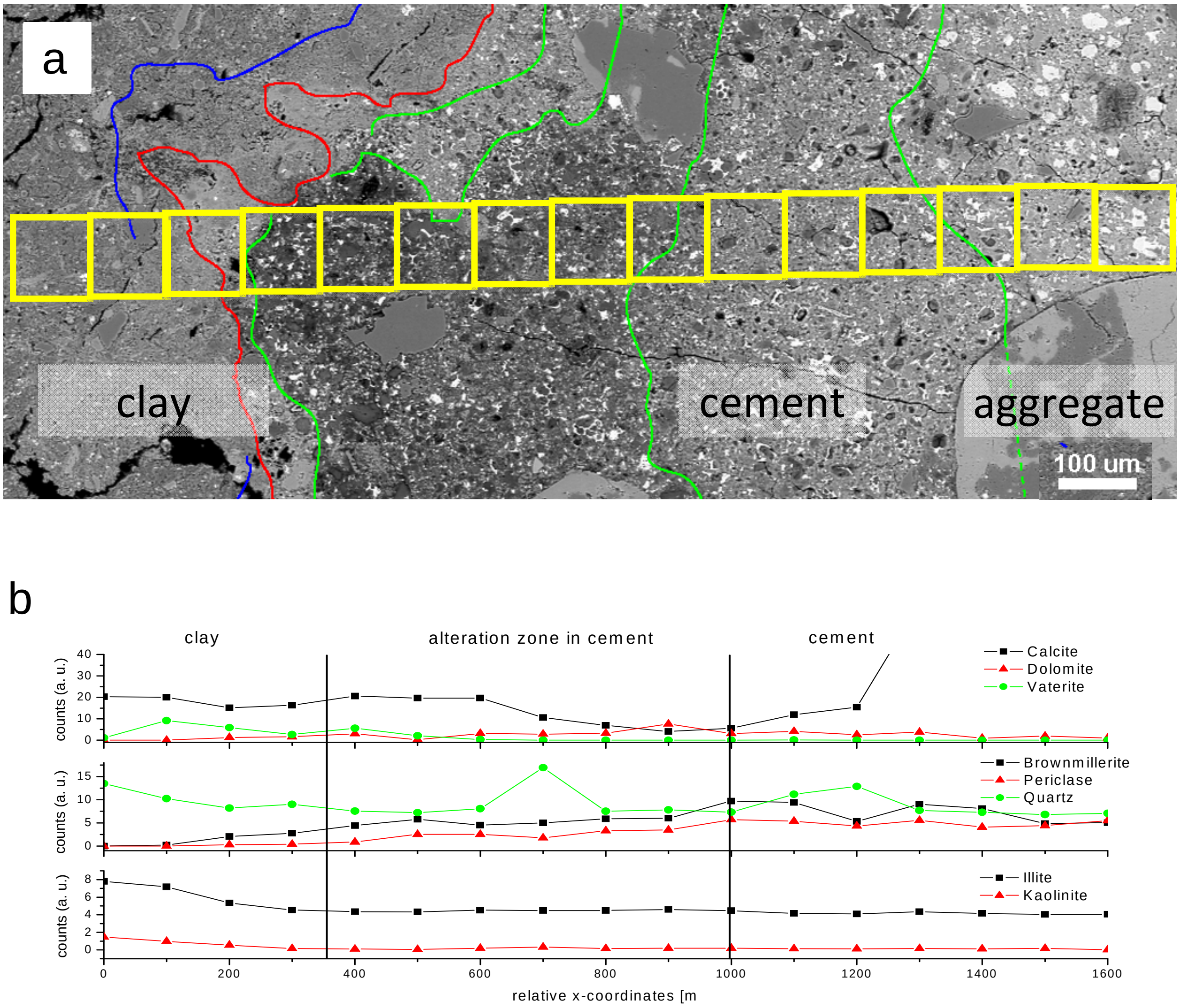

Fig. 1. a) SEM image of the cement-clay interface aged for two years. The squares indicate the positions for which XRD measurements were performed. The red line marks the cement/OPA interface. The blue and green lines indicate various sub-zonations. b) Semi quantitative analyses based on characteristic XRD reflections.

Publication

Dähn, R., D. Popov, Ph. Schaub, P. Pattison, D. Grolimund, U. Mäder, A. Jenni, E. Wieland (2014). X-ray micro-diffraction studies of heterogeneous interfaces between cementitious materials and geological formations. Phys. Chem Earth. 70-71, 96-103.