Study of stylolites using Laser Induced Breakdown spectroscopy

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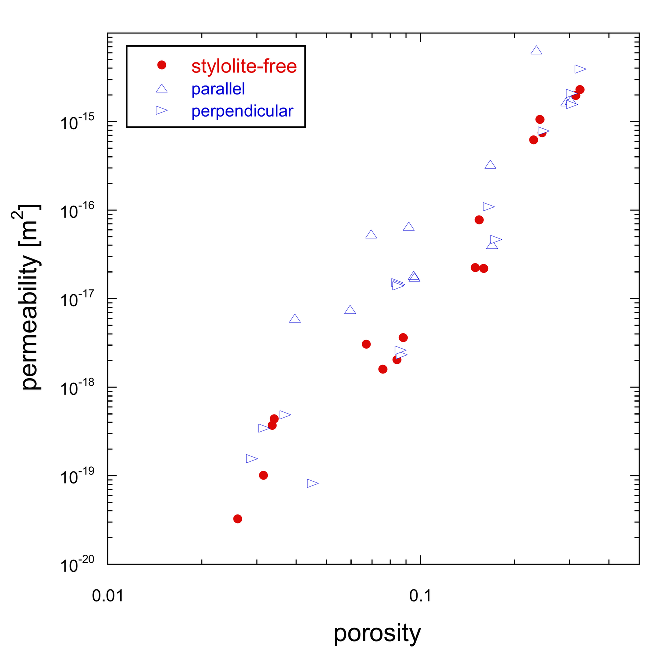
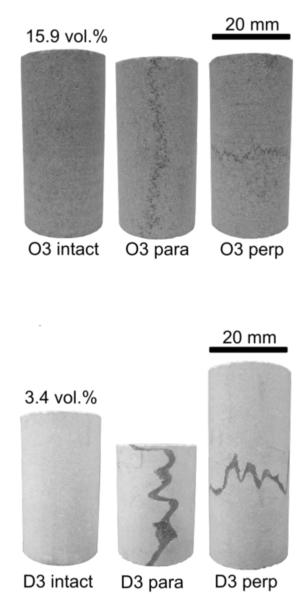
INTRODUCTION

Stylolites are the product of intergranular pressure-solution and are common in sedimentary rocks, such as carbonates, sandstones, and shales. They appear as column-and-socket interdigitation features and are filled with insoluble elements such as organic matter, oxides, or clay particles. Knowledge of their impact on fluid flow in reservoir rocks is an important consideration in many facets of geosciences. For decades, widespread opinion, inferred from a variety of petrographic analyses and borehole logging data, suggest that stylolites act as permeability barriers. However, experimental studies to date showed that stylolites in limestones do not in fact influence permeability when they are oriented perpendicular to fluid flow (Heap et al., 2014). To the contrary, existing data rather suggested that stylolites could be conduits for fluid flow. This was however difficult to prove unambiguously. An alternative to permeability measurements would be to compare the chemical composition of the host rock and the stylolites, looking for differences, and in particular elements in the stylolite absent from the host rock. In this study, we performed such systematic chemical analysis on samples of limestone using Laser Induced Breakdown Spectroscopy (LIBS).

PERMEABILITY DATA



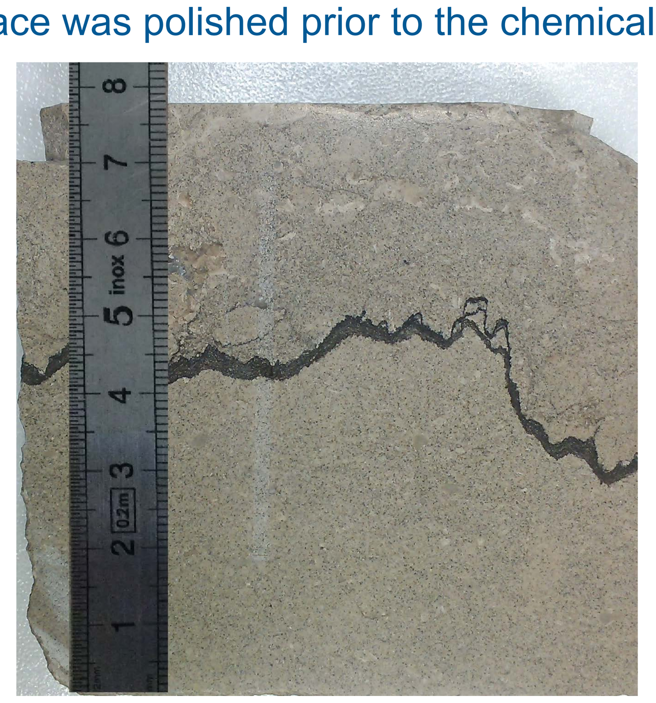


Compilation of permeability on carbonates from Lind et al. (1994), Heap et al. (2012) and Rustichelli et al . (2015). Measurements were performed on stylolite-free samples and on samples with a stylolite oriented parallel and perpendicular to flow (blue triangles). When oriented orthogonal to flow, stylolites had no effect on permeability.

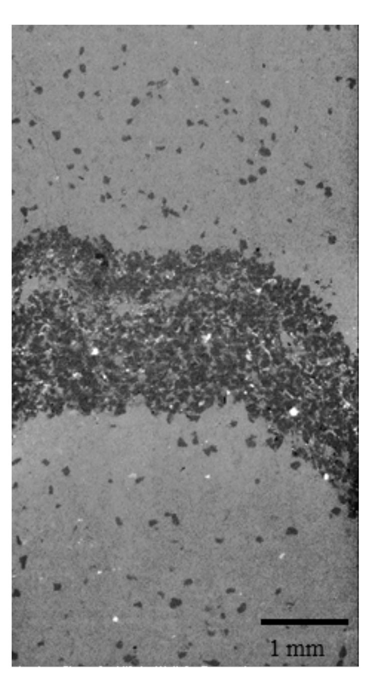
MATERIAL AND LIBS ANALYSIS

In this study we used cores from limestone formations surrounding the ANDRA Underground Research Laboratory (URL) at Bure in the south of the Meuse district, France. We selected the samples of Dogger limestone used Heap et al. (2014). The porosity of the host rock was measured to be 3.4% and the thickness of the stylolite was found between 1.5 and 3 mm. The sample surface was polished prior to the chemical analysis.

a)



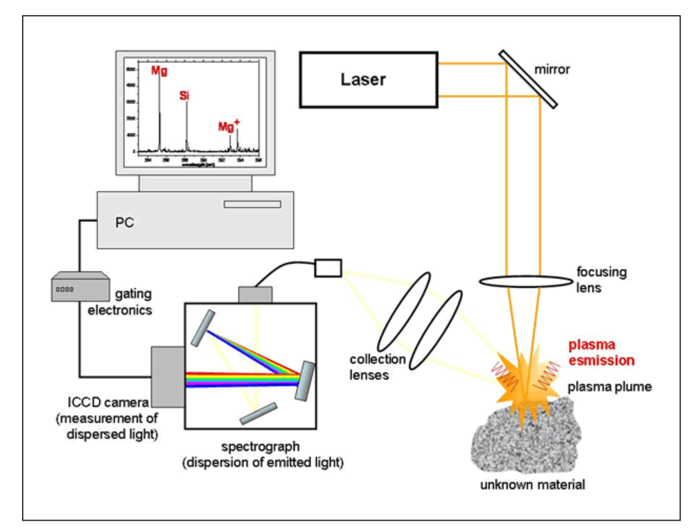
b)



(a) Studied stylolite in a limestone of Dogger age. (b) X-ray Computed microtomography data (CT) with 4 µm resolution on the same sample. The thickness of this part of the stylolite was about 2 mm. Quartz grains appear darker in the CT data.

LIBS consists of a laser source for the sample ablation, a spectrometer for the emission signal detection connected to an optical fiber, a CCD camera and optical lenses to focus the beam on the sample and to collect the emitted light on the spectrometer entrance. After the ablation, a micro-plasma is created and the excited electron emits photons. Then, the collected spectrum provides an elemental analysis. The system can detect, identify and quantify the chemical composition of any geological material. In this study, we used two LIBS systems. Measurements were first performed using a portable system at Epitopos (Strasbourg), a company which is using the LIBS to analyse artworks, monuments during restoring, or find gold or silver ores in the mining industry. Samples were positioned at a distance of 12 cm in front of the laser. 50 shots were taken at a frequency of 10 Hz, each 5 mm starting from the stylolite and moving up and down. The spectral resolution was 0.1 nm and the spot size was 150 µm. Some chemical maps were also realised in the laboratory of the CRITT Matériaux Alsace. We used a second non portable LIBS system with a range of wavelength of 200 nm. The chemical maps were made between 250 and 300 nm with a gain of one.

a)

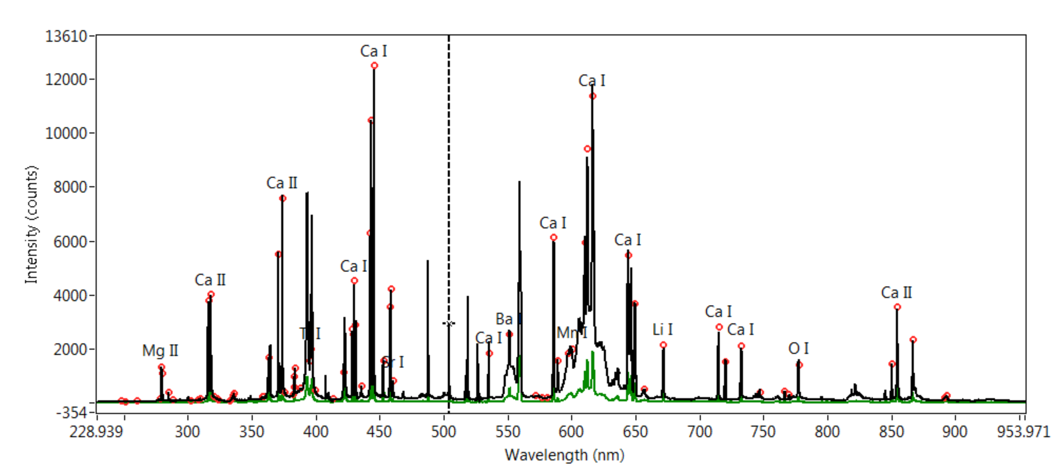


b)

a) A typical laboratory LIBS set-up (from https://www.uni-muenster.de/Planetology/en/ifp/research/geologischeplanetologie/LIBS.html). b) Photograph of the LIBS system of Epitopos.

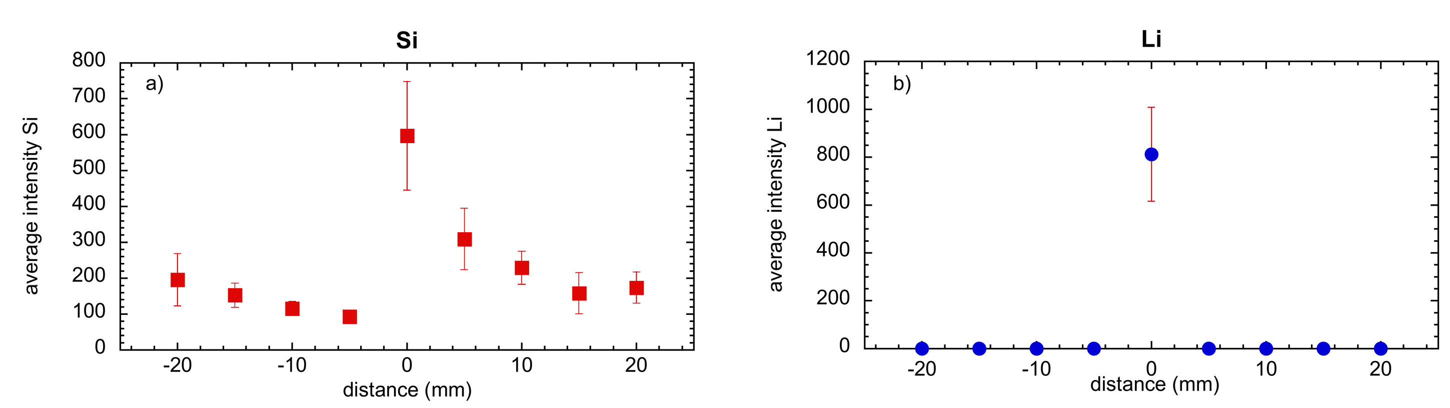
RESULTS

Typical spectrum for Dogger limestone showed a large number of peaks which corresponds to different element (Figure 2). For example, the peak at 445 nm is representative of calcium, consistent with the fact that Dogger limestone is mostly composed of calcite (more than 95%). The analysis showed that the limestone contained a large number of other elements (Ca, Na, Mg, K, Fe, Si, etc.) both in the host rock and the stylolite. We also noticed the presence of a peak of lithium (Li) at 670,423 nm with high intensity only in the stylolite.

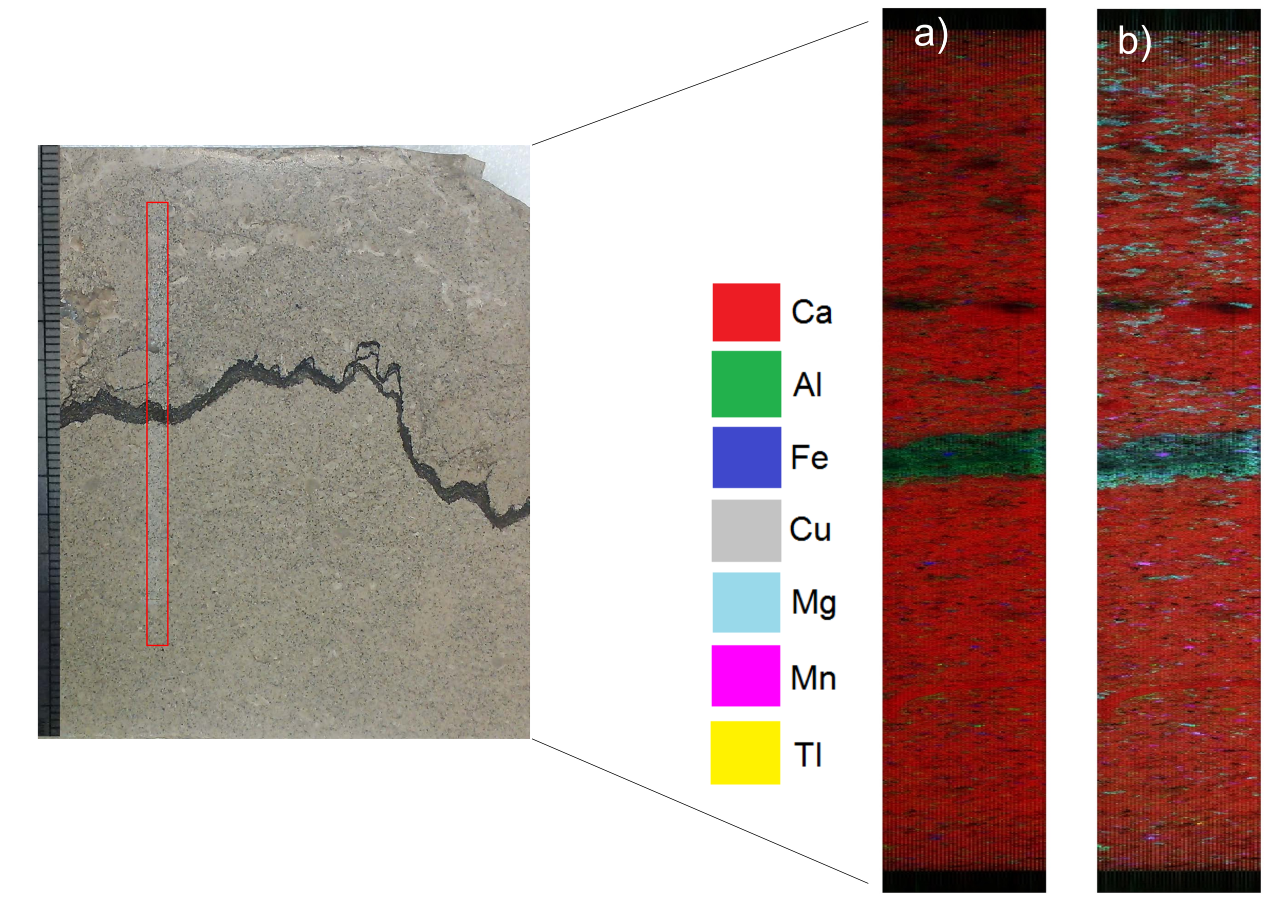


Example of spectrum on the Dogger limestone for a single shot (black) and an average of 50 shots (green). Peaks of calcium (Ca) and magnesium (Mg) are visible at this scale. Zooming on such data gave the precise composition of the sample.

Average intensities were determined for each detected element.



Average intensities of (a) silicon, (b) lithium in Dogger limestone as a function of the distance to the stylolite.



Chemical maps by LIBS of a sample of Dogger limestone between wavelengths of 250 nm and 300 nm: (a) Ca, Al, and Fe, (b) Ca, Al, Cu, Mg, Mn and Ti. Silicon and lithium were not visible in this range.

CONCLUSIONS

In this study, we showed that it is possible to reproduce the complex structure of a stylolite by performing chemical mapping using LIBS. With LIBS, such chemical analysis was easier and significantly faster than using standard techniques involving Scanning Electron microscopes. LIBS also presented the advantage to potentially reveal light elements. Our new data indeed revealed the presence of lithium in the stylolite, while this element was not found in the host rock. Together with permeability measurements on the same samples (Heap et al., 2014) and recent porosity mapping and data from Mercury Capillary Injection Pressure (Baud et al., 2016), our results suggest that the stylolites in the Dogger limestone could act as conduit for fluid flow. In the future, more analysis by LIBS will be performed on stylolites from other carbonate formations.

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