Lithium tracking in different limestones containing stylolites using Laser Induced Breakdown Spectroscopy

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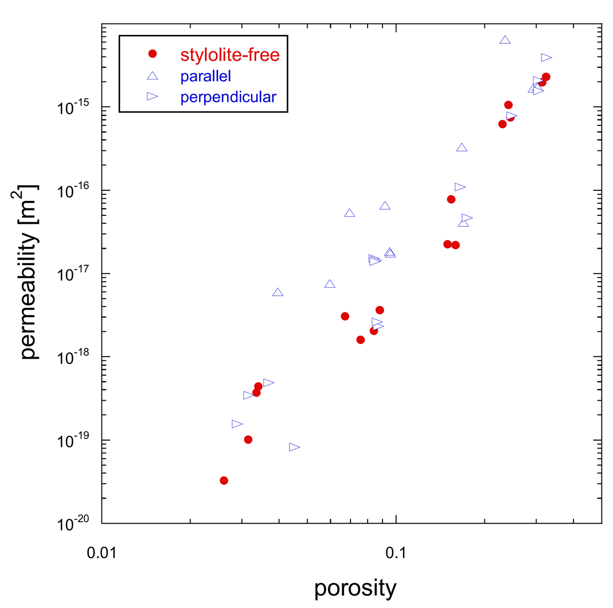
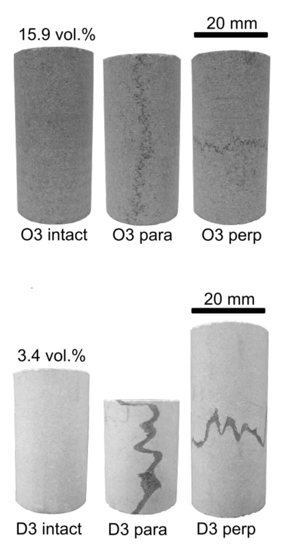
Photography encouraged

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; 2018). 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



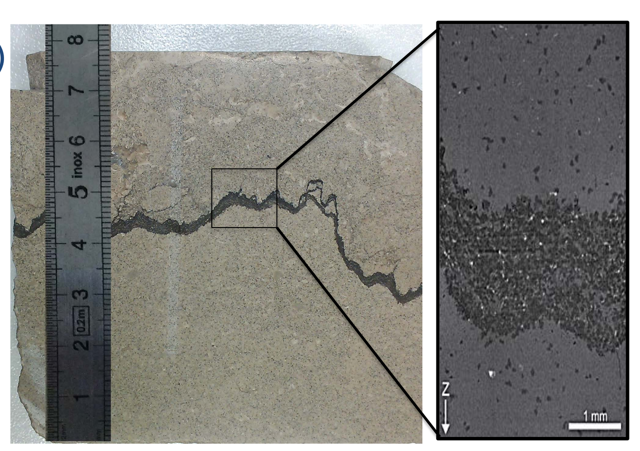


Compilation of permeability data on carbonates from Lind et al. (1994), Heap et al. (2012) and Rustichelli et al. (2015). Measurements were performed on stylolite-free samples and on samples with a stylolite oriented parallel and perpendicular to flow (blue triangles). When oriented orthogonal to flow,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

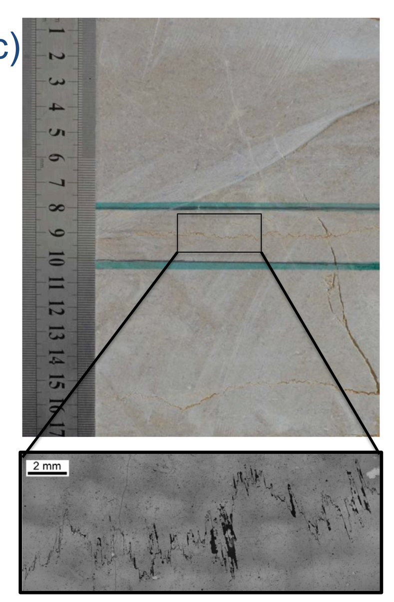
Materials and LIBS analysis

In this study we used cores from Dogger and Oxfordian limestone formations surrounding the ANDRA Underground Research Laboratory (URL) at Bure (France). Blocks from Comblanchien and Corton limestone formations provided by the Rocamat quarry located next to Beaune in France, were also studied. We studied the samples previously selected by Heap et al. (2014; 2018). The porosity of the host rock was measured to be between 2.5 and 3.5% for Dogger, Comblanchien and Corton limestones but raised up 15.4 % for Oxfordian limestone formations. The thickness of the stylolite was found between 1.5 and 3 mm for Dogger limestone but did not exceed 200 µm for the other limestones. The sample surface was polished prior to the chemical analysis.

a)



c)



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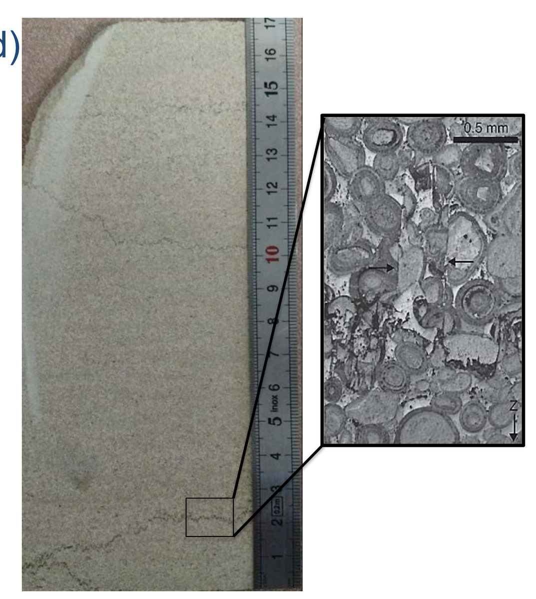

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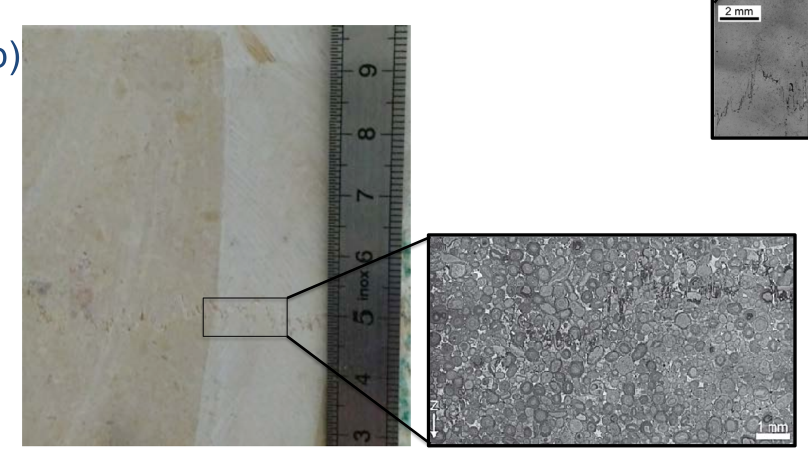
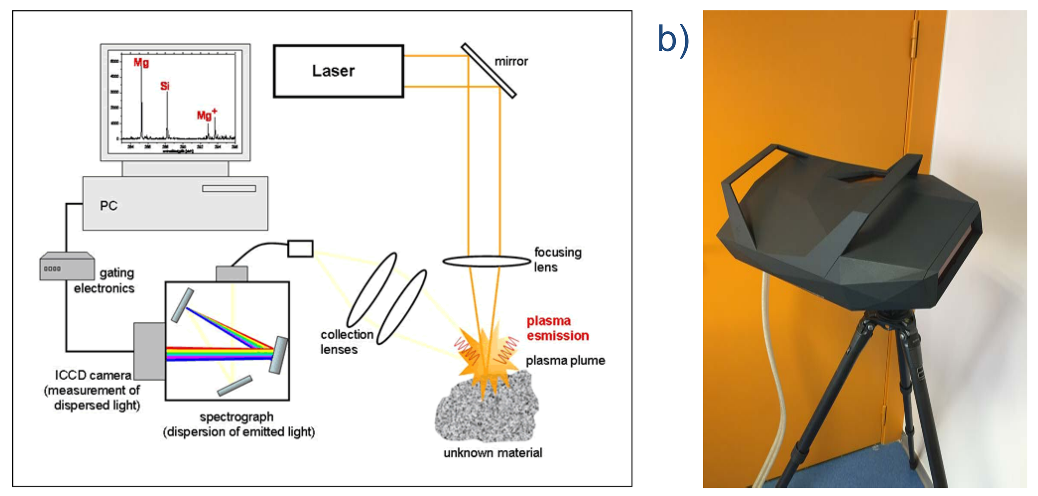


Pictures of the studied stylolites and X-ray Computed microtomography data (CT) with 4 µm resolution for (a) Dogger, (b) Comblanchien, (c) Corton and (d) Oxfordian limestones. Denser areas appear lighter in the CT data.

LIBS consists to point a laser beam on a surface sample. After the ablation, a high-temperature micro-plasma is created and the exited electrons emitted photons during their return to there steady state. The light is collected by a fiber and injected into a spectrometer. A light emission spectrum gives the intensity of specific wavelengths. This gave us an elemental analysis of the material. Measurements were first performed using a portable system at Epitopos (Strasbourg), a company which is using the LIBS to analyse artworks during restoring or find 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.

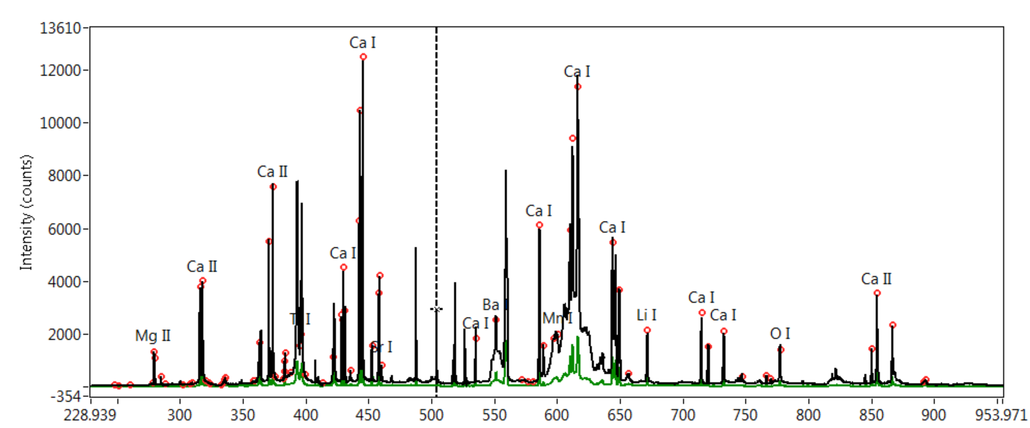
a) b)



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.

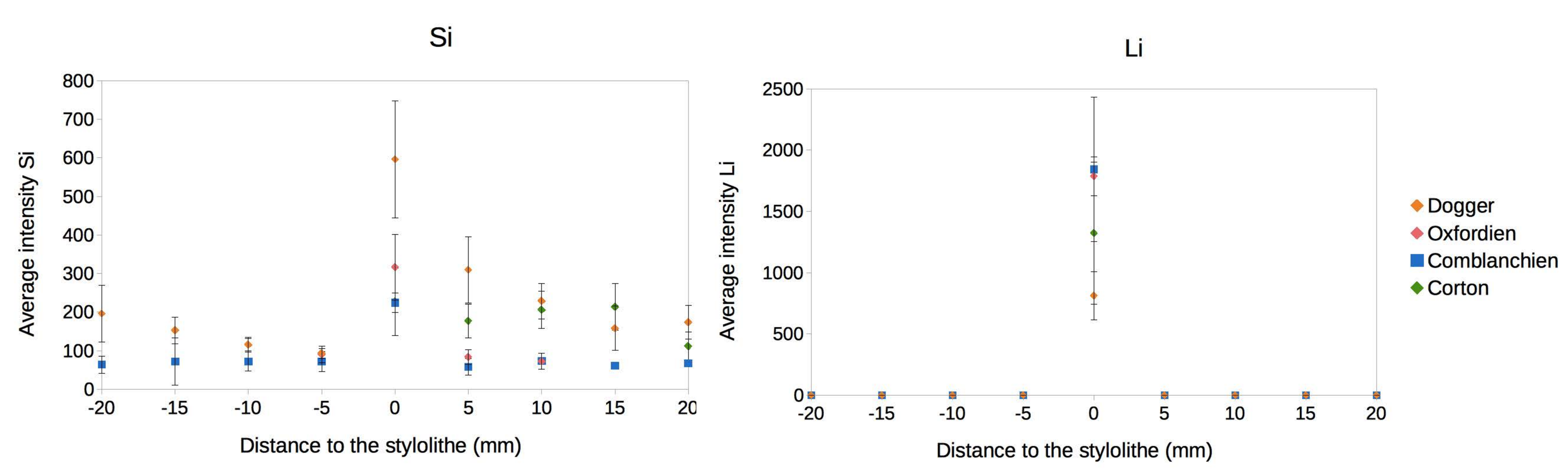
Results

Typical LIBS spectrum for studied limestones showed a large number of peaks which corresponds to different element. For example, the peak at 445 nm is representative of calcium, consistent with the fact that limestones are mostly composed of calcite (more than 95%). The analysis showed that samples 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 only in the stylolite of the different samples studied.



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.

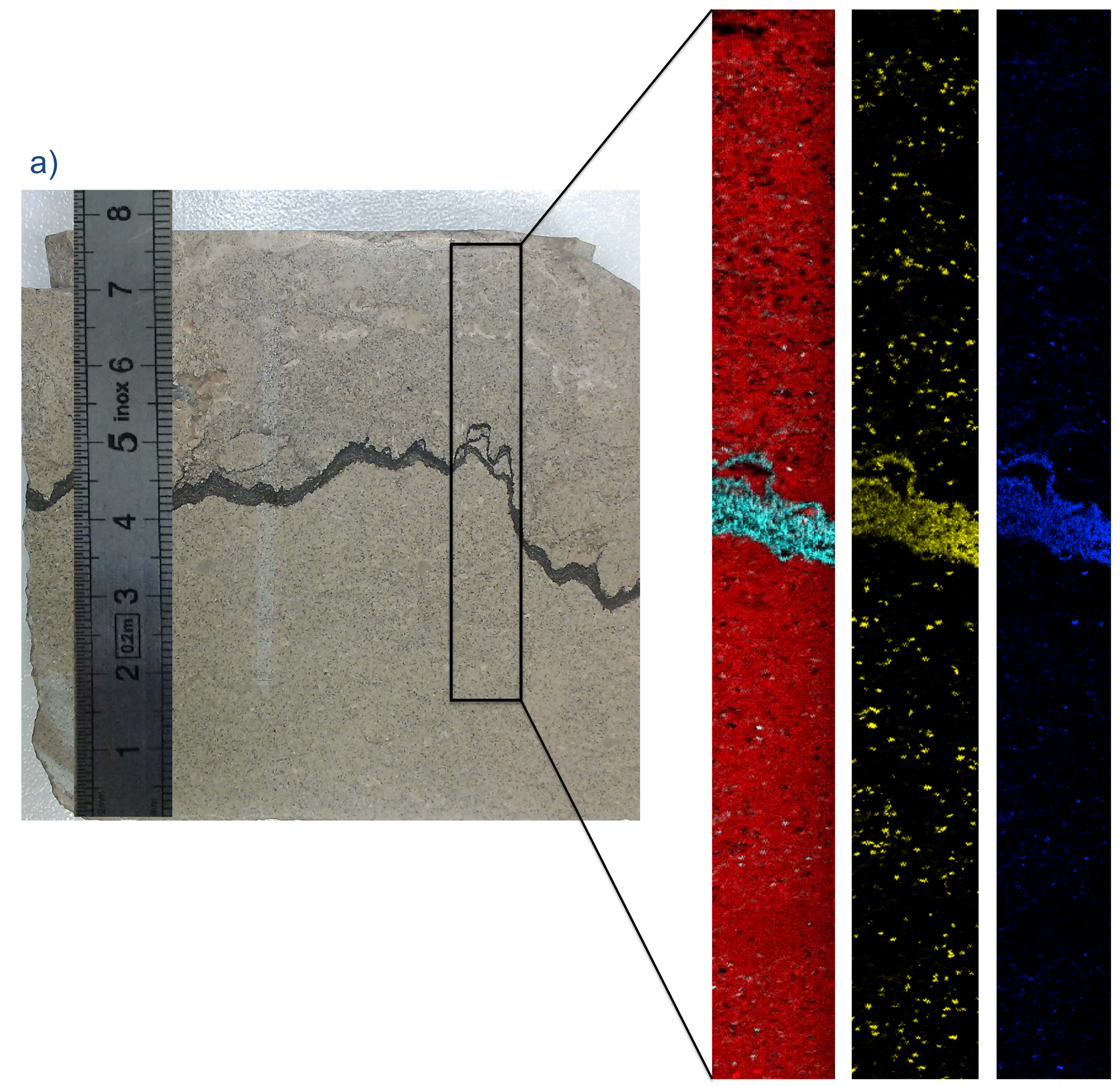
Average intensities were determined for each detected element for the Dogger, Oxfordian, Comblanchien and Corton limestones.



Average intensities of (a) silicon, (b) lithium in Dogger, Oxfordian, Comblanchien and Corton limestones as a function of the distance to the stylolite.

Additionally, we showed that it is possible to see the geometry of the stylolites by performing chemical mapping using LIBS. For Dogger, Oxfordian, Comblanchien and Corton limestones, stylolites contain less calcium but are enriched in silicon, aluminium and lithium.

a)



a) Chemical maps by LIBS of Dogger limestone between wavelengths of 250 nm and 300 nm.

Ca

Li

Si

Al

Conclusion

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; 2018), porosity mapping and data from Mercury Capillary Injection Pressure (Baud et al., 2016), our results suggest that the stylolites in the Dogger, Oxfordian, Comblanchien and Corton limestones could act as conduit for fluid flow in carbonates. More work will be done to discuss the possible origin of the lithium found in the stylolites and to precisely quantify the amount in each studied stylolite.

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