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

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Stylolites are the product of intergranular pressure-solution and are common in sedimentary rocks. They appear as column-and-socket interdigitation features and are filled with insoluble elements. 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. To the contrary, existing data suggested that stylolites are conduits for fluid flow. An alternative to permeability measurements could be to compare the chemical composition of the host rock and the stylolites, looking for 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).

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, measurements were 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 for 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. A delay time between the laser pulse and the recording was necessary in order to avoid capturing the plasma. The spectral resolution was 0.1 nm and the spot size was 150 μm. The spectrum collected was in a range of 230 nm to 900 nm. The average spectrum of each point, the intensity of some selected chosen elements and the noise intensity were noted and then ratios, enabling to determine the presence/absence of elements and variations in terms of composition.

We studied samples from four limestone formations from Meuse and Burgundy (France), with porosity ranging from 3 to 15%. 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. Indeed, our new data revealed the presence of lithium in the stylolite, while this element was not found in the host rock. We discussed the possible origin of Lithium in the stylolites of the studied formations. LIBS detection limit seems to be low for atomic elements and to this end, the next step will be to determine precisely the calibration scale for lithium.