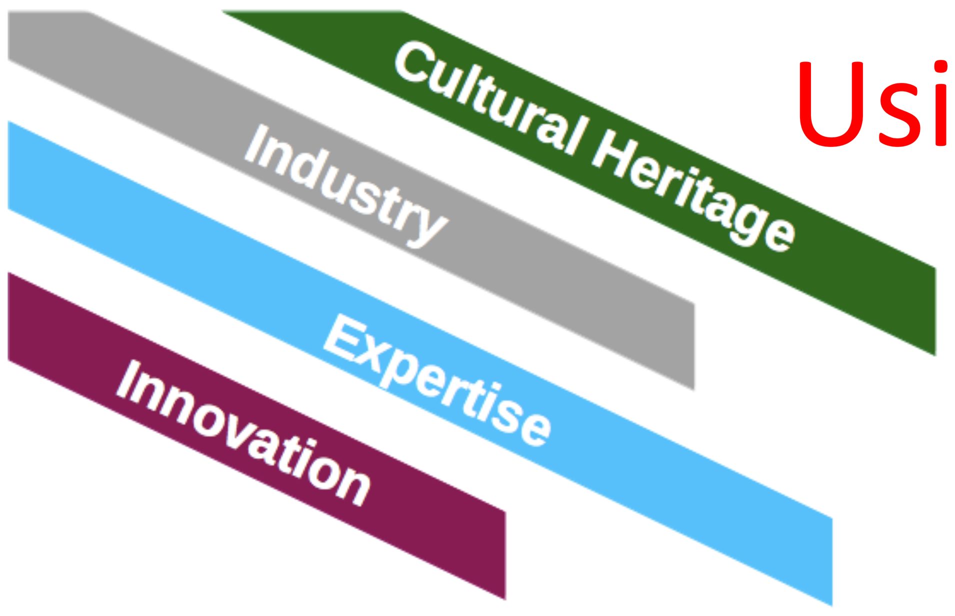

Using LIBS to study Lithium silicate penetration for stone consolidation

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Introduction

In the field of cultural heritage, stone alteration induces significant damages and that is why it is necessary to find solutions to preserve the rock durability. Consolidants agents such as ethyl silicate are often used. It is a process which rebuilds contacts between grains by filling pore spaces with a fluid susceptible to solidify. Our study consists to determine the penetration depth of a new kind of binding agent called lithium silicate using Laser Induced Breakdown Spectroscopy (LIBS). It has the advantage to be insoluble in water and does not release volatile compounds (such as ethyl silicate which releases ethanol). Besides, the consolidant creates silica and lithium carbonate (A. Thorne 2012). This product is composed of lithium that is hard to detect with traditional methods. However LIBS technology can detect low atomic weight elements such as hydrogen, boron or lithium in different types of material (P. Baud 2018) and could allow us to follow the penetration depth of lithium silicate.

The aim of this study is to detect the lithium silicate penetration depth into different kind of rocks coming from different kind of monuments : sandstones from Strasbourg cathedral, limestones from Vincennes castle and limestones from Tournus city hall.

LIBS principle

The Laser Induced breakdown Spectroscopy (LIBS) is an innovative technology used to analyse the elemental composition of materials and pigments (Grégoire et al. 2012). It consists to point a laser beam on a surface sample (Fig.1-3). 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 fiber and injected to a spectrometer. A light emission spectrum gives the intensity of specific wavelengths. This provide us an elemental analysis of the material.

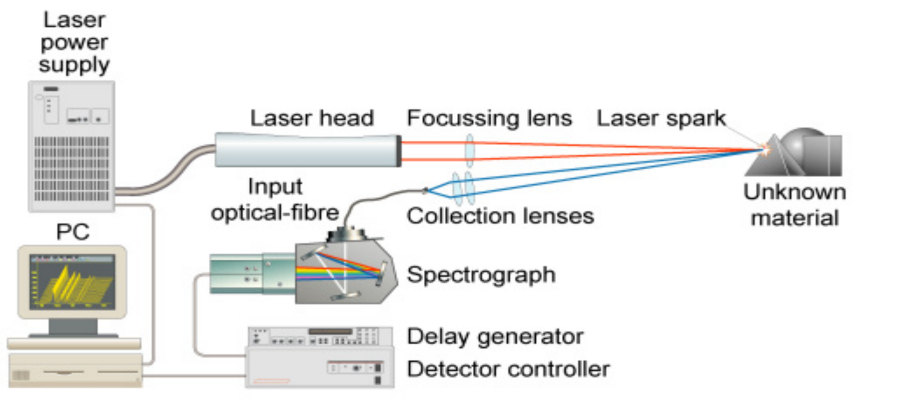

Fig.1 : Principle of LIBS. A laser beam is focused on a surface sample and a generated plasma is recorded by a spectrometer. Spectra obtained permit to determine the sample composition (A.I Whitehouse)

Fig.2 : Portable LIBS system used by Epitopos

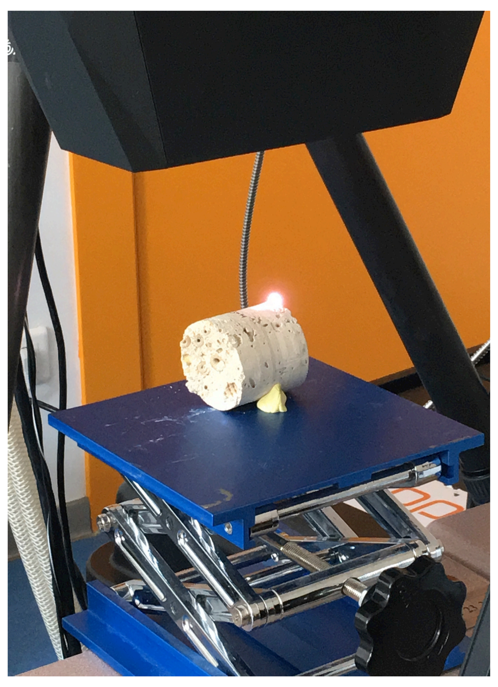

Fig.3 : LIBS shots on a limestone sample

Methodology

The samples used for this study (Fig.4) included limestones (two from Tournus and five from Vincennes) and sandstones (two from Strasbourg cathedral) whose petrophysical parameters (diameter, length, porosity, sound speed propagation and density) were determined in laboratory.

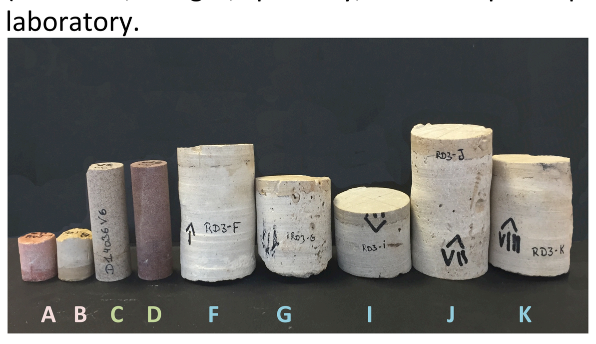

Fig.4 : Samples impregnated with the binding agent. A-B: Tournus limestones, C-D: Sandstones, F-K: Vincennes limestones.

Fig.5 : Lithium silicate impregnation

Measurements of capillarity and capillary rises (Fig.5) were realised after lithium silicate impregnation according to NF EN 1925 standard.

Besides, the nine samples were analysed by LIBS before and after impregnation with lithium silicate. Shots were performed on the surface and along the cores. For each sample, 50 shots were performed at each point with a frequency of 5Hz. On the surface, 4 areas were analysed before (in blue) and after (in red) impregnation (Fig.6). Shots every 1, 2, 5, 10, 15, 20, 30 and 40 mm along a line were performed. At the end, 8 lines were studied : 4 before (in blue) and 4 after (in red) lithium silicate impregnation (Fig.7).

With the collected spectrum obtained by LIBS, intensities of lithium, potassium (the reference present in each rock) and calcium were determined at the surface and for each depth before and after impregnation. The lithium pic used is at 670.823nm, the potassium at 766.393nm and the calcium at 671.717nm. The intensity of the calcium pic is taken into account because it is close to the pic of lithium and could influence the intensity value. In order to obtain the real lithium pic intensity, we removed the intensity of the calcium and the noise. For the potassium, we also removed the noise to obtain the real intensity.

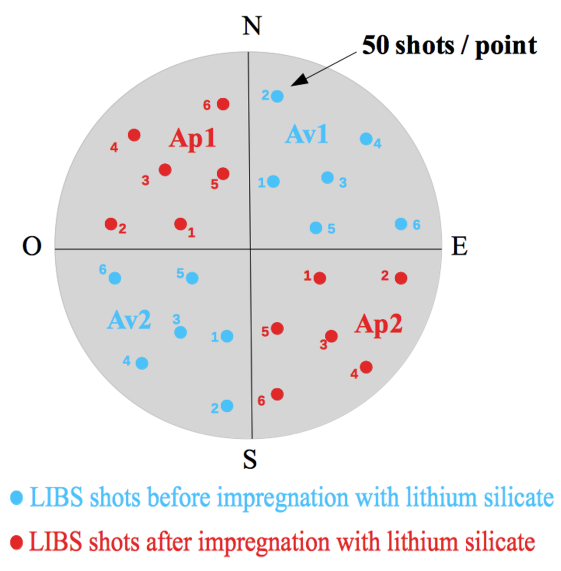

Fig.6 : Surface of each sample. Areas analysed by LIBS before (in blue) and after (in red) impregnation with lithium silicate.

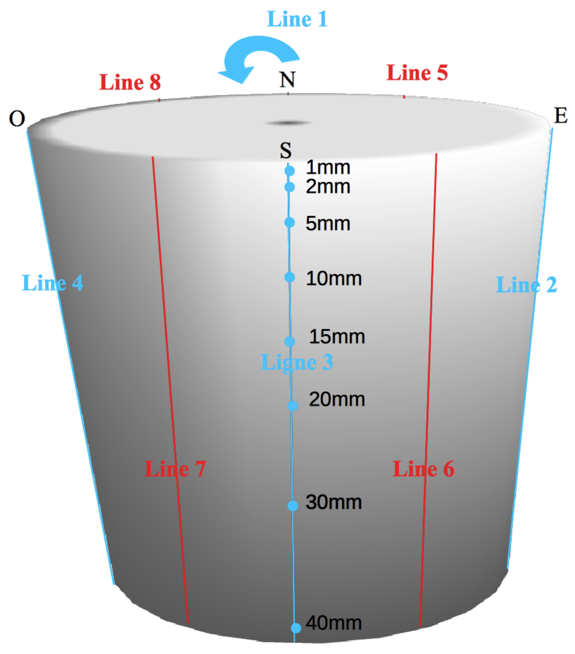

Fig.7 : Lines along the core. Lines analysed by LIBS before (in blue) and after (in red) impregnation with lithium silicate.

Results

Before impregnation

The petrophysical parameters determined in laboratory provide information about the link between porosity and sound speed propagation. Indeed, the velocity increases when the porosity decreases (Fig.8). This could be explained by the higher sound speed propagation in rocks than in the air.
Intensity ratios of lithium on potassium are plotted against the depth for Tournus (Fig.9) and Vincennes limestones (Fig.11) and for Strasbourg Cathedral sandstones (Fig.10). The results show that ratios against the depth are relatively constant and the same (between 0.10 and 0.60) for each sample even if porosities are different.

References	Diameter (mm)	Length (mm)	Porosity (%)	Vp (m/s)	ρ (kg/m³)
D18000RD3-A	20	20	10	/	2455
D18000RD3-B	20	20	6	/	2557
D18000RD3-C	20	55	17	4007	2183
D18000RD3-D	20	55	17	3818	2206
D18000RD3-F	43	60	17	3700	2246
D18000RD3-G	43	40	19	3230	2192
D18000RD3-I	43	35	11	4350	2424
D18000RD3-J	43	68	16	4770	2294
D18000RD3-K	43	50	18	3790	2227

Fig.8 : Petrophysical parameters (diameter, length, porosity, sound speed propagation velocity and density) of each sample. A-B: Tournus limestones, C-D: Sandstones, F-K: Vincennes limestones.

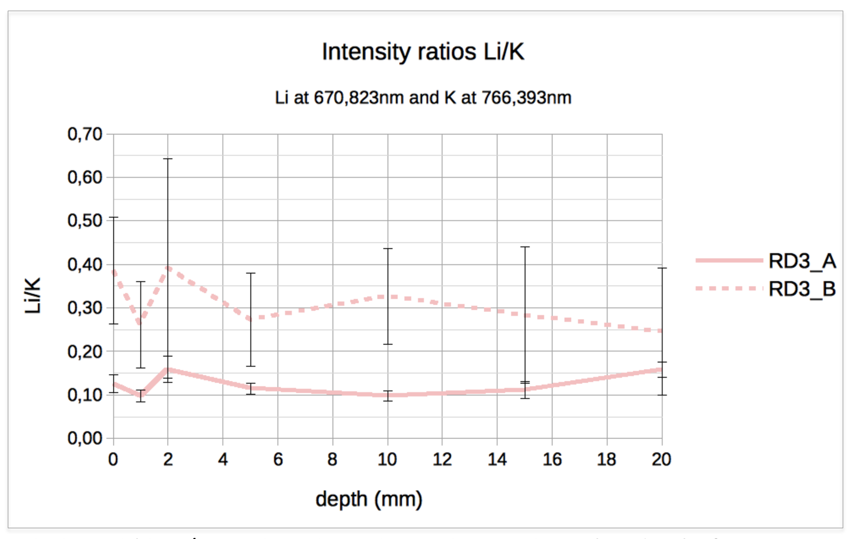

Fig.9 : Lithium/potassium intensity ratios against the depth for Tournus limestones.

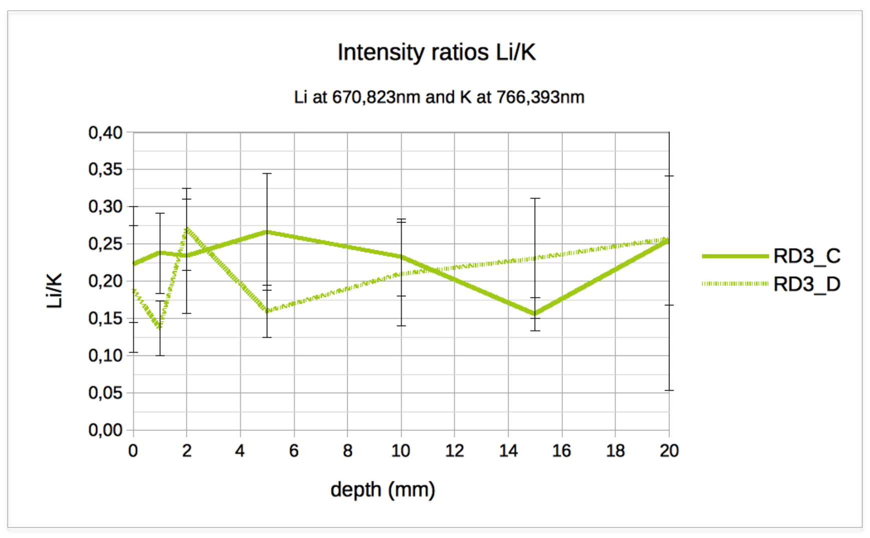

Fig.10 : Lithium/potassium intensity ratios against the depth for the sandstones

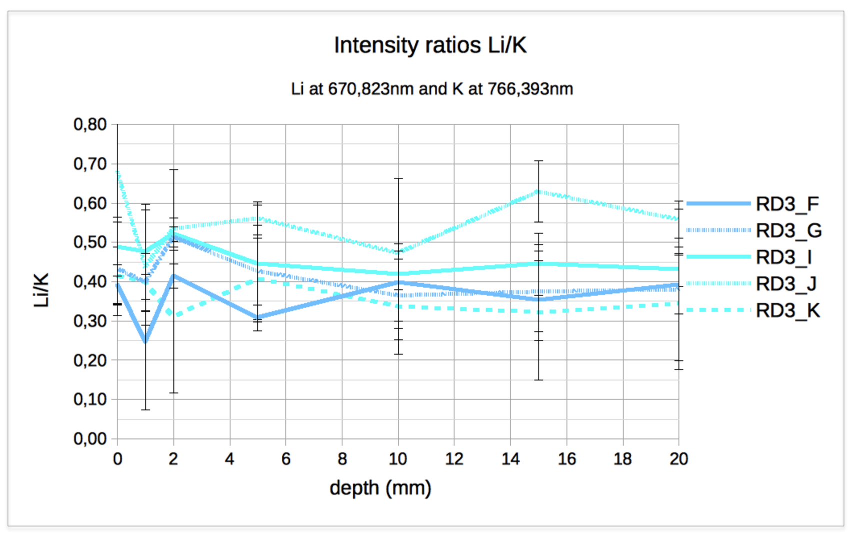

Fig.11 : Lithium/potassium intensity ratios against the depth for Vincennes limestones.

Before impregnation, lithium is detected in the three types of rock but in low content. No relation between the porosity and the initial lithium concentration in the limestones and sandstones studied could be determined.

After impregnation

Intensity ratios of lithium on potassium are plotted against the depth for the Tournus (Fig.12) and Vincennes limestones (Fig.14-15) and for Strasbourg cathedral sandstones (Fig.13). Capillarity and capillary rises are determined too (Fig.16-17). The results show that capillary rises are higher in sandstones than in limestones (14 mm against 5 for Tournus and 8 for Vincennes). Limestones from Tournus and I,J from Vincennes seem to have low capillarities (1-3). We can also notice that the capillarity coefficient changes with the depth before reaching the constant level for F,G,K limestones from Vincennes and the sandstones. Besides, lithium is detected after the capillary fringes and decreases quickly after the fringe for Tournus and J limestones but slowly after the fringe for F,G,I,K limestones and the sandstones.

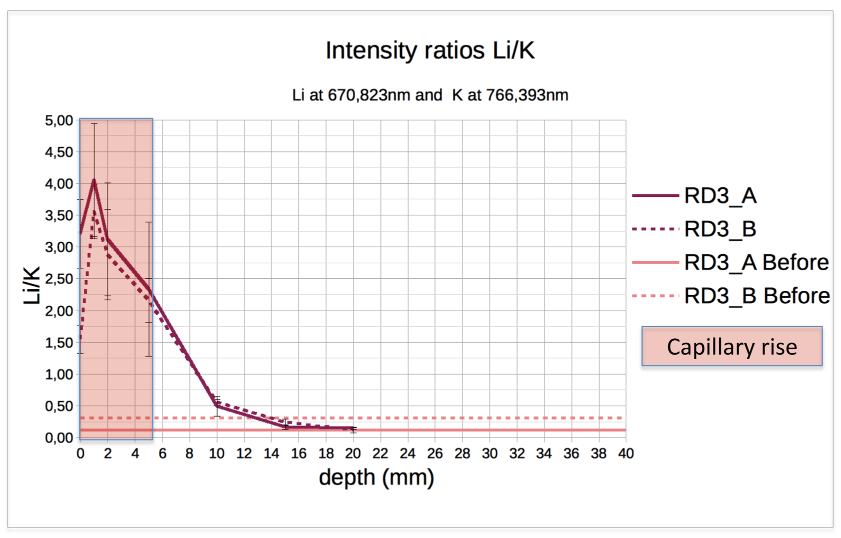

Fig.12 : Lithium on potassium intensity ratios against the depth for Tournus limestones.

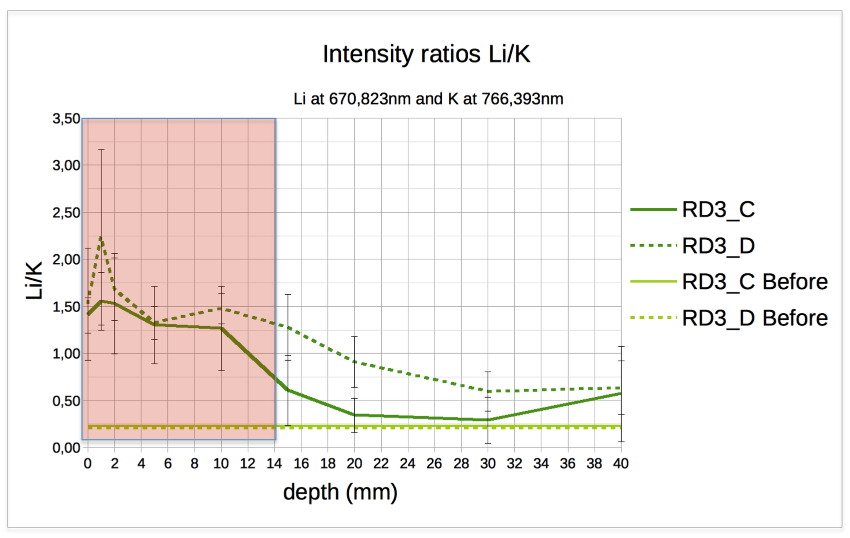

Fig.13 : Lithium on potassium intensity ratios against the depth for the sandstones

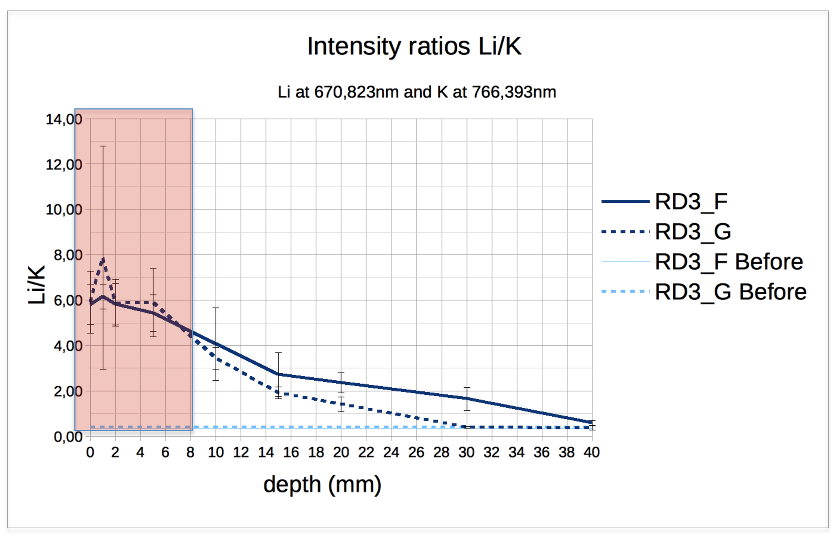

Fig.14 : Lithium on potassium intensity ratios against the depth for Vincennes limestones.

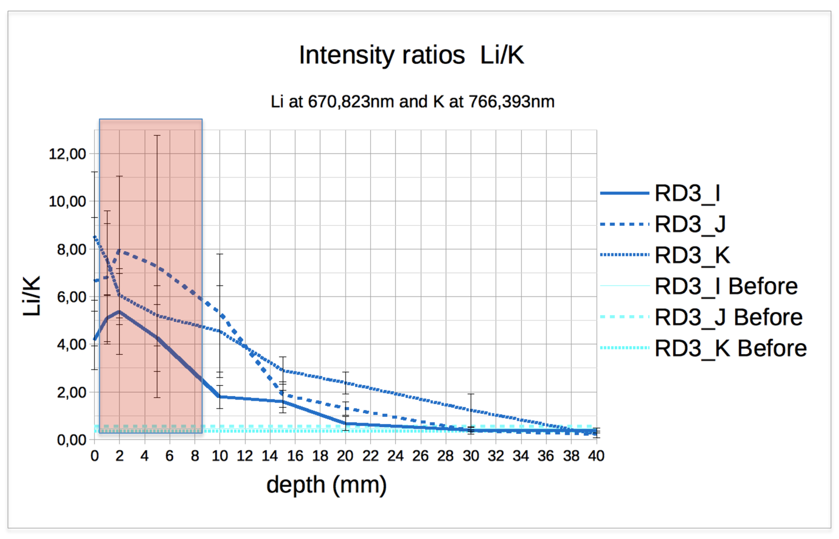

Fig.15 : Lithium on potassium intensity ratios against the depth for Vincennes limestones.

References	Capillary height (mm)	Capillarity ($g.m^{-2}.s^{-1/2}$) (slope)		Correlation coefficient R	
D18000RD3-A	4.5	2.54		0.99	
D18000RD3-B	5.5	1.89		0.99	
D18000RD3-C	13	9.99	3.18	0.99	1
D18000RD3-D	18.3	32.83	2.58	0.99	0.99
D18000RD3-F	9.5	11.07	3.91	0.98	0.99
D18000RD3-G	7.5	6.80	1.61	0.98	0.99
D18000RD3-I	5.8	2.06		0.99	
D18000RD3-J	8.5	3.92		0.98	
D18000RD3-K	9.5	8.48	3.36	0.98	1

Fig.16 : Capillarity values and capillary heights.

After impregnation, lithium is detected in the three types of rock in higher content than before (3 to 10 times more). Besides, lithium depth penetration is higher in sandstones which have a higher capillarity and is detected after the capillary fringe in each rock.

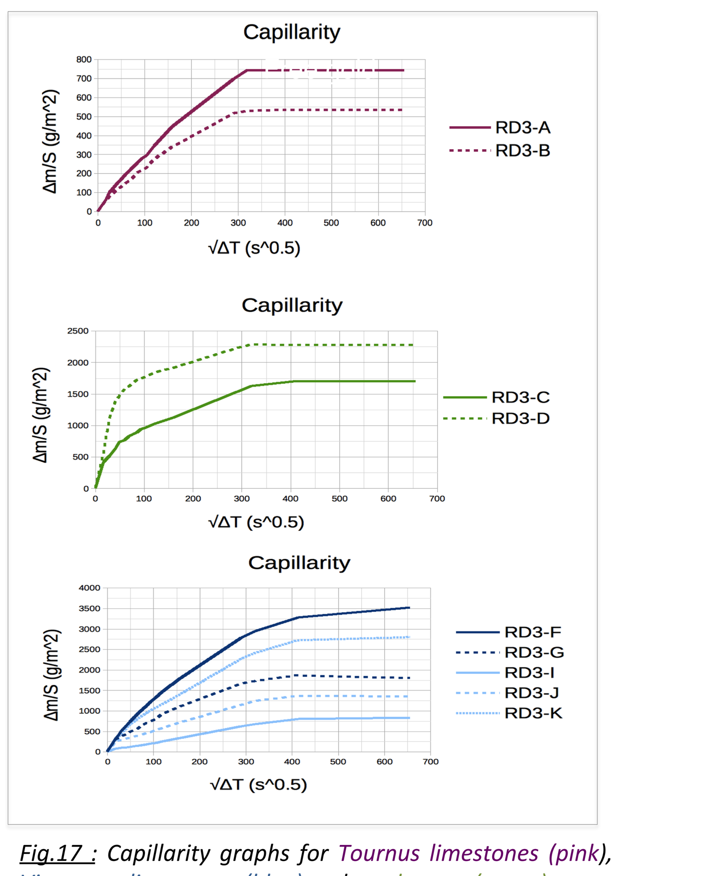

Fig.17 : Capillarity graphs for Tournus limestones (pink), Vincennes limestones (blue) and sandstones (green).

Discussion

LIBS results show that the penetration depths are different for each rock. For sandstones with a high capillarity (10-30), the penetration depth is important (14 mm approximately) but for rocks with lower capillarity, the penetration is lower (5 mm for Tournus and 8 mm for Vincennes limestones). LIBS also detects lithium after capillary fringes which probably means that the consolidant effect goes deeper than the fringe. Indeed, ratios decrease quickly after the capillary fringe for rocks with a low capillarity (Tournus and J limestones have their capillarities between 1 and 3). But ratios decrease slowly after the capillary fringe for rocks which have the capillarity that changes with the depth before to reach the constant level (as the sandstones and F,G,K limestones).
Few researches have been done on lithium in sandstones or limestones so we have no references about lithium content in rocks. The methodology works only if the initial lithium concentration in rocks is low. If the content is to high, LIBS spectra will be saturated and no differences before and after lithium silicate impregnation will be seen.
LIBS technology allows us to detect lithium in three types of rock coming from different monuments (castle of Vincennes, Cathedral of Strasbourg and Tournus city hall) and to follow the penetration of lithium silicate consolidant. This study shows LIBS advantages and applications in the cultural heritage. Indeed, the technology can detect low atomic weights elements which are difficult to discern with other methods such as hydrogen, boron and lithium. It can be used on field to limit the number of samples collected and needs no sample preparation (A.I Whitehouse). The last advantage of LIBS is that the data processing can be done on field and the results can be used instantly by architects or conservators.

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