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Visualisation of ethyl silicate consolidant in pore space of porous building stones using microscopic methods

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ABSTRACT: The consolidation of porous stones using ethyl silicate has a long-term practice in the field of conservation. In the present study three Neogene porous building stones (a limestone, a volcanic tuff, and a calcareous sandstone) from Hungary were selected and consolidated with ethyl silicate using a vacuum-circulation (VAC) method. Drilling core samples taken from the test blocks were investigated by different microscopic methods, such as polarising microscopy, cathodoluminescence microscopy, and scanning electron microscopy. Based on the observations it can be stated that especially the cathodoluminescence and scanning electron microscopy are eligible for an exact and unambiguous 2- and 3-dimensional visualisation of the amorphous solid consolidant in the pore space of the stone. The results have shown that the distribution of large gel fragments with shrinkage cracks is different, irregular, and mostly limited to the sub-surface zones in all three stone types. The results of the microscopic observations were compared to drill resistance and ultrasound transmission velocity data, resulting from the measurements carried out before and after the consolidation. The preliminary comparison has not shown clear correlation between the optical observations and the values of mechanical measurements. The results thus suggest that changes in bulk mechanical properties after the treatment do not necessarily correlate with the real places of precipitation and especially with the binding capacity of the consolidant.

Key words: consolidant, visualisation, microscopic methods, porous stones, silica gel

1 INTRODUCTION

Conservation of deteriorated stone by impregnation with inorganic or organic consolidant fluids is a long-term practice. However, several decisive factors such as the depth of impregnation, the exact place of solid precipitation, the binding capacity, and finally the microstructure of the consolidant in the pores have been inadequately studied. This lack of knowledge is probably due to the fact that only few analytical methods are capable of localising and identifying the precipitated consolidants in the pore space of stones. Thus, the efficacy of a consolidation treatment is usually assessed through measurements of bulk mechanical properties of the stone before and after treatment (Pápay & Török, 2006, 2007). Well-established methods are based, e.g. on the ultrasound transmission velocity and the drill resistance in depth. Both procedures are generally useful and yield quantitative results, but they fail to provide clear information about the above mentioned key parameters and thus about the effect of the consolidant on a mineral material.

Microscopic methods, on the other hand, provide mainly information of a semi-quantitative type, but allow localising and visualising the consolidants (Alvarez de Buergo et al., 2003). Possible methods are e.g. polarising microscopy (PM), scanning electron microscopy (SEM), and cathodoluminescence microscopy (CL). Each of the above techniques has its benefits and specific abilities and can therefore be combined in order to carry out successful investigations.

The aim of the present study is to test the combined use of polarising microscopy and scanning electron microscopy linked with energy-dispersive X-ray analysis, and cathodoluminescence microscopy for their potentials to detect silicate precipitated from an ethyl silicate treatment in the pore space of a porous limestone. Drill resistance and ultrasound velocity measurements have been carried out before and after the consolidation on the same stone sample in order to compare them with the optical visualization and obtain the information about their accuracy and effectiveness.

2 EXPERIMENTAL

2.1 *Stones, products, treatment*

The study was performed on the so-called Sóskút "Coarse" Limestone, i.e. a porous biogenic oolitic limestone of Upper Miocene (Sarmatian) age from Sóskút near Budapest. Its total porosity ranges from 25 to 40 % by volume. On the turn of the 20th century this type of stone played an important role in Budapest and Central Hungary in the building operations and restoration works (e.g. the Parliament House, the Matthias Church, the Opera House, several public buildings, etc.). Notwithstanding the widespread use of this stone, its low resistance to environmental stresses such as acidic rain and freeze-thaw cycles was well known since the first half of the 20th century (Láczay, 1944). The main degradation processes can be ascribed to sulphuric acid attack on the microcrystalline calcium carbonate cement, followed by the formation of thick gypsum crusts and loosening of the fabric, as well as loss of material behind the nearly impermeable crust (Láczay, 1944; Török & Rozgonyi, 2004).

In addition some preliminary results of two other test consolidated porous stones will be presented in this paper. The Upper Miocene (Badenian) grey, biotitic and soft rhyolite tuff (the so-called Eger Tuff), with dacite and andesite bearing volcanoclastics is widely spread in North Hungary and partly on the Great Hungarian Plane since the Middle Ages.

The Budafa Sandsone is yellowish grey sandstone of shoreline, plain shore and delta facies from the Lower Miocene (Karpathian). Its main area of application is found in South Hungary.

In the frame of the international Culture2000 project "VAC-Method", several Central European stone types - among others the three Hungarian stones mentioned above - have been test consolidated in order to evaluate the efficiency of the VAC (Vacuum-circulation strengthening) method. The project has been described by Pintér & Horváth (2007).

The consolidation tests have been carried out on blocks of slightly altered limestone of approximately 25x30x40 cm, originating from the historical limestone quarry by Sóskút, from the Mediaeval Castle of Eger (tuff), and from the Cathedral of Pécs (sandstone). The treatment was performed using an ethyl silicate product (Funcosil KSE 300 by Remmers of Germany, with a gel concentration of about 300 g/l), commonly used for the consolidation of porous limestones and sandstones in Central Europe. Immediately after the treatment one of the blocks was cut into two pieces in order to control the penetration depth of the solution. In the case of the Hungarian stones, from 3 cm (tuff) to full penetration (Sóskút Limestone) of the Funcosil 300 was stated.

In order to detect the efficacy of the treatment the ultrasound transmission velocity and drill resistance of the cores were measured before and after the consolidation. The data have been compared to the results of optical observations.

2.2 *Sampling and analytical methods*

Two months after the treatment (the period which, according to the producer, should suffice for the precipitation of the solid consolidant) cylindrical core samples with a dimension of 4x20 cm were taken from the test blocks. The blocks were gently cut alongside into two parts: one of them was impregnated under vacuum with a low-viscous resin containing a blue dye. Polished thin sections of standard 30 μm thickness were prepared for the petrographic, scanning electron microscopic, and cathodoluminescence analyses. Broken sample chips were taken from different depths of the other half of the core for the SEM analysis.

Optical observations and textural analysis were carried out in plane- and cross polarised light using a Nikon SMZ 1500 (up to 100x) and an Olympus BX-40 (up to 1000 x) polarising microscope.

SEM observations were carried out under high vacuum at 20 kV using a Philips XL30 ESEM scanning electron microscope fitted with an energy-dispersive X-ray analytical system LINK (EDX).

Cathodoluminescence examinations (CL) were performed using a Reliotron cold-cathode equipment mounted on a Nikon Eclipse E600 polarising microscope and operated at 7-9 kV accelerating voltage and 0.6 to 0.9 mA current. The same microscopic section was used for all three optical methods.

3 RESULTS

3.1 *Optical microscopy*

The fabric of Sóskút limestone is composed of small spherical to slightly ellipsoidal ooids with a diameter of 100 to 1000 microns. They have regular concentric $CaCO_3$ laminae developed around different detrital nuclei, mostly mono- and polycrystalline quartz, feldspar, or rock fragments. The ooids are cemented with fine-grained microsparitic radial-fibrous calcite cement (Fig. 1). The samples also contain some bioclasts such as e.g. mollusc and foraminifer fragments. Based on the systems of Folk (1962) and Dunham (1962), the Sóskút limestone can be classified as an oobiosparite, grainstone.

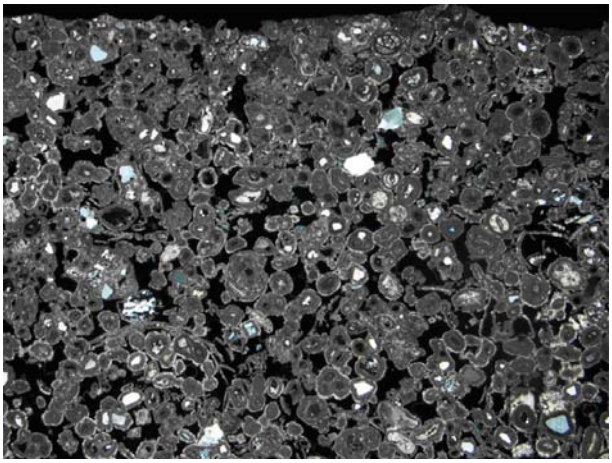

Fig. 1. Thin section image of Sóskút limestone (crossed polars). Width of image: 2 cm.

Microscopic observations clearly show the porous structure of the analysed stone type: between the ooids large primary intergranular macro pores of a size up to 2 mm can be observed. Within and between the clasts also smaller capillary pores are observable.

Using the petrographic microscope one could not unambiguously detect the solid silica gel consolidant in the pore space of the samples. This is due to the optical properties of the material: the low birefringence and the glassy, amorphous structure did not allow exact identification of the colourless silica gel in the pores.

The volcanic Eger Tuff contains quartz, feldspar, plagioclase, and biotite phenocrystals in a glassy matrix (Fig. 2). Pumice and volcanic rock fragments are also common inclusions in this rock type. The identification of silica gel in the pores could not be performed. Gel fragments and glassy matrix of the tuff exhibits the same optical properties respectively: obtained with parallel polars both materials are colourless with similar birefringence. Because of their isotropic optical properties in crossed polars they both show extinction.

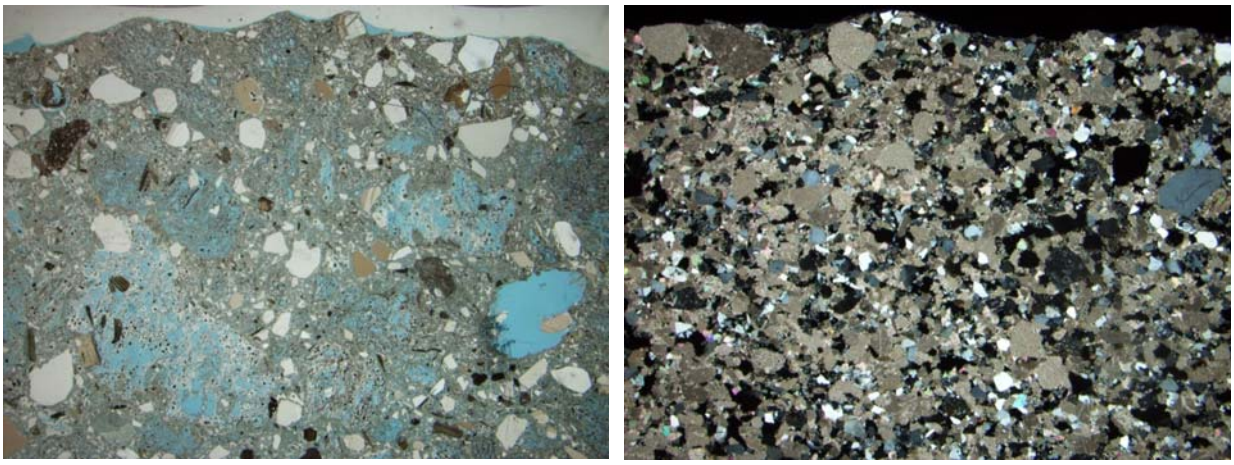

Fig. 2-3. Thin section image of Eger Tuff (parallel polars) and Budafa sandstone (crossed polars). Width of images: 2 cm.

The Budafa Sandstone is a lithic greywacke, where the matrix consists of sparitic calcium carbonate. Common minerals are: quartz, feldspar, mica (muscovite and biotite), and amphibole (Fig. 3). Rock

fragments are also abundant: volcanic rock fragments, limestones, and clayey rock fragments are the most common lithic clasts. Some larger gel fragments in the sub-surface pores could be detected using the polarising microscope.

The use of a blue dye during the preparation process of the sample can help to find and identify the gel fragments. This method, however, could not be used efficiently enough.

3.2 *Cathodoluminescence microscopy*

Calcite in the Sóskút limestone exhibits bright orange-red CL with homogenous distribution (Figs. 4 and 5). The luminescence is caused by Mn^{2+} substitution in the structure, which is the most important activator in carbonate minerals (Marshall, 1988).

Blue-green CL colours of the consolidants with moderate and bright intensity (Figs. 4 and 5) can be related to intrinsic luminescence centres, e.g. structural defects and/or extrinsic luminescence centres related to impurities incorporated into the silica structure. Natural analogues of the consolidants are hydrated amorphous SiO2 phases like opal. Opal can exhibit variable blue CL colours caused by varying Al contents (Götze et al., 2001). In the case of consolidants structural defects as well as Sn, the catalyser used to promote consolidation can activate CL emission. Further CL spectral studies are planned to detect the exact nature of the luminescence centres.

The use of the CL microscopy made unambiguously possible the visualisation in 2D the solid silica gel consolidants. Due to the characteristic luminescence colour which allowed an easy and prompt identification of the consolidant in the pore space of the limestone, the amount, distribution, shape, and size of the silica gel could also be exactly identified. The size of the large gel fragments varies be tween 20 and 100 microns. They mostly form amorphous small crusts and fragments around the calcite cement with typical micro cracks and drying shrinkages (Figs. 4 and 5).

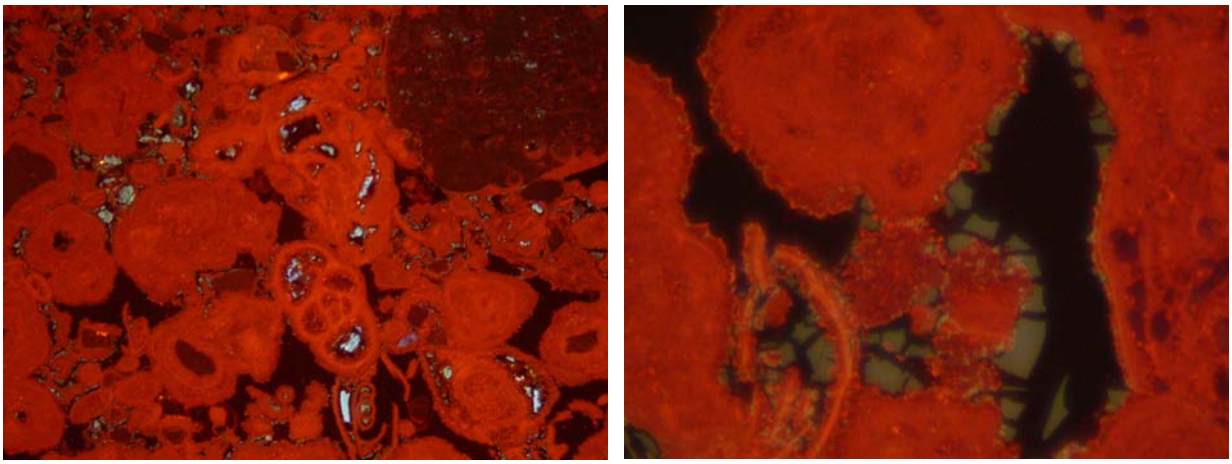

Fig. 4-5. CL images of Sóskút limestone (width of image: 2 mm (left) and 0.5 mm (right)).

In the sub-surface of the sample we have found a zone of approximately 2 mm thickness with large amount of precipitated silica gel. Below this zone, i.e. up to a depth of 10 cm, the distribution of the gel seems to be irregular in all samples.

Larger gel fragments have only precipitated in zones of smaller pore radii (20 to 150 μm), in secondary voids, or sometimes within intragranular pores (Fig. 4 and 5).

No evidence for silica gel bridges between adjacent ooid grains was found.

Preliminary CL results of Eger Tuff and Budafa Sandstone show similar features of the silica gel to those that it was found in the Sóskút Limestone. The characteristic blue-green CL colours allow distinguishing the consolidant from the minerals, such as carbonate, quartz, feldspars, etc. of the stones. Especially in the case of the porous tuff could be good results observed: small (5 to 50 μm) silica gels were homogeneously distributed in the pores of the glassy matrix (Figs. 6 and 7). Based on the observation a penetration depth of max. 1 cm could be unambiguously detected.

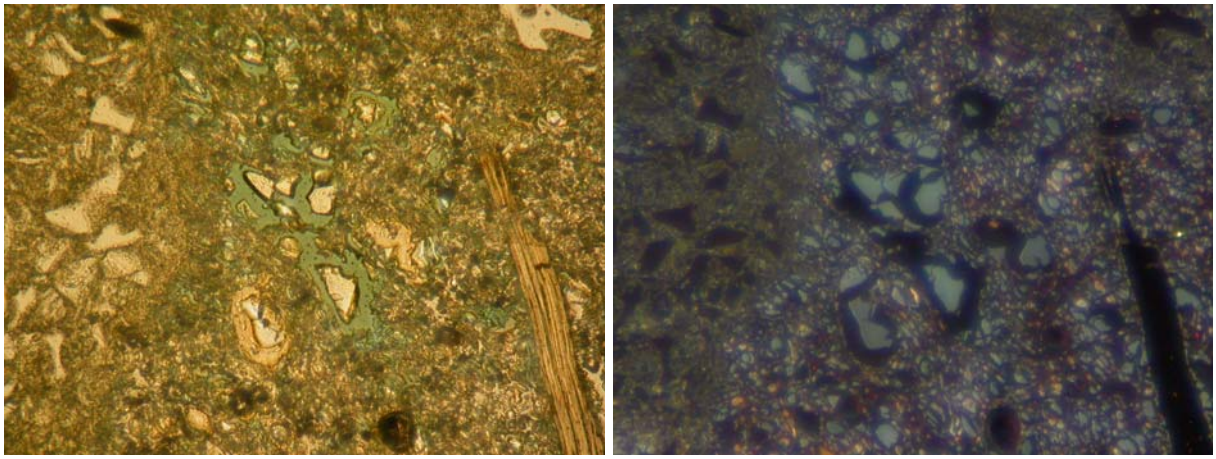

Fig. 6-7. Silica gel fragments in plane polarized light (left) and CL image of Eger Tuff (width of image: 2 mm).

The size and distribution of the consolidant in the Budafa Sandstone also exhibits similar features to the features mentioned above, however the amount, size, and distribution of gel fragments were larger than it was found in the limestone and in the tuff. In the sub-surface pores has large amount of consolidant accumulated which could either refer to the fast precipitation rate of the KSE and/or to the over-consolidation of the surface zone (Figs. 8 and 9).

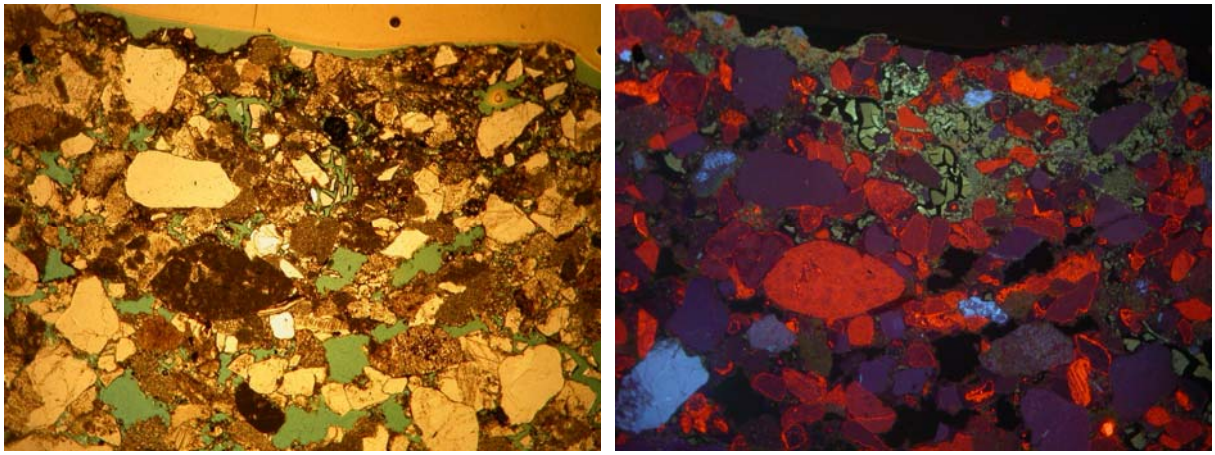

Fig. 8-9. Silica gel fragments in plane polarized light (left) and CL image of Budafa Sandstone (width of image: 4 mm).

3.3 *Scanning electron microscopy*

In this paper only the SEM results of the Sóskút Limeston will be presented. The SEM-BSE analyses on polished thin sections confirmed the results of the CL observations. Based on the CL results, large gel fragments with shrinkage cracks could be easily detected, especially in the zones near the surface (Fig. 10) and within intragranular pores (Fig. 11). Using the optical advantages of the scanning electron microscope, further observations could also be carried out.

At high magnifications, very thin gel coatings of the dimensions 1 to 10 μm could be observed in small capillary pores and on the surface of the radial-fibrous calcite cement of the ooids. Similarly to the larger gel fragments, the surface of this thin film has also revealed drying shrinkages.

Three-dimensional SEM-SE visualisation of the film on broken surface samples also supported this observation. This thin coating covers homogenously the ooids and can be found in each sample (Fig. 12).

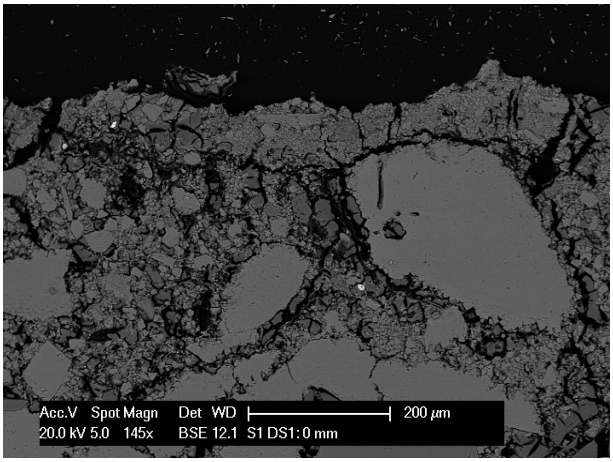

Figure 10. SEM-BSE image of treated Sóskút limestone at the very surface, showing coarse aggregates of silica gel (dark grey clasts) in pores.

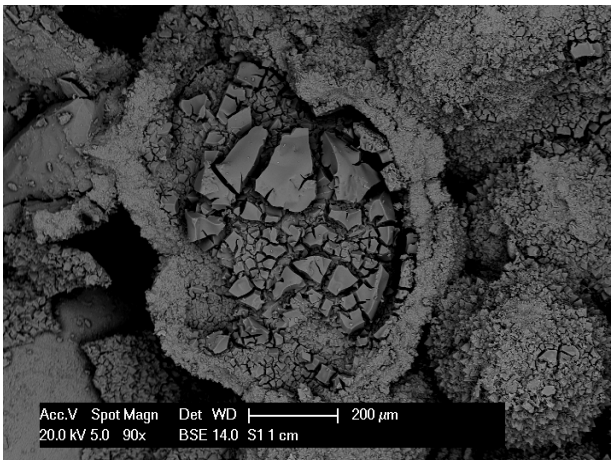

Figure 11: SEM-BSE image of treated Sóskút limestone showing the inner void of an ooid filled with silica gel; no consolidant in intergranular pores.

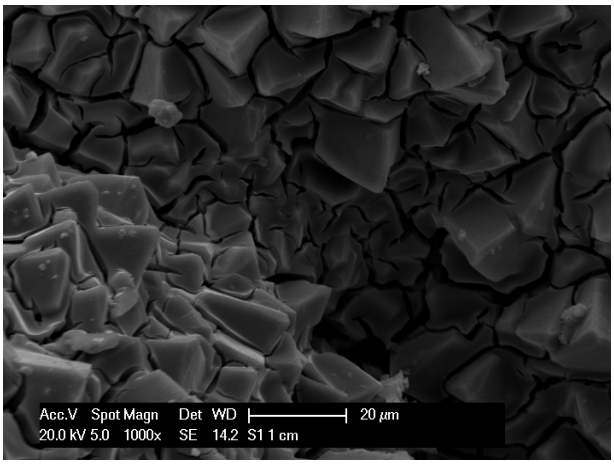

Fig. 12. SEM-SE image, showing silica gel coating on the surfaces of sparitic cement

The SEM evidence also did not reveal silica gel bridges between the adjacent grains in smaller pores. The presence of Sn in the gel fragments measured by SEM-EDX refers to the presence of a catalyser used to promote consolidation after the penetration.

4 COMPARISON OF ULTRASOUND TRANSMISSION VELOCITY AND DRILL RESISTANCE DATA WITH OPTICAL OBSERVATIONS

The comparison of optical observations, such as size and distribution of silica gel in pore space of the test consolidated stones with ultrasound transmission velocity (US) and drill resistance (DR) values provided similar results in the case of all three stone types. Generally it can be stated that drill resistance values correlate better with the optical observations than ultrasonic transmission velocities. Nevertheless, drill resistance results show in the most cases only limited correlations too.

In the case of Sóskút Limestone CL observations showed clear precipitation of the consolidant in the sub-surface zones, however ultrasound transmission values have not shown any significant increase in this depth. The increase of drill resistance force in the sub-surface zone of the sample may refer to the presence of precipitated silica gel (Fig. 13).

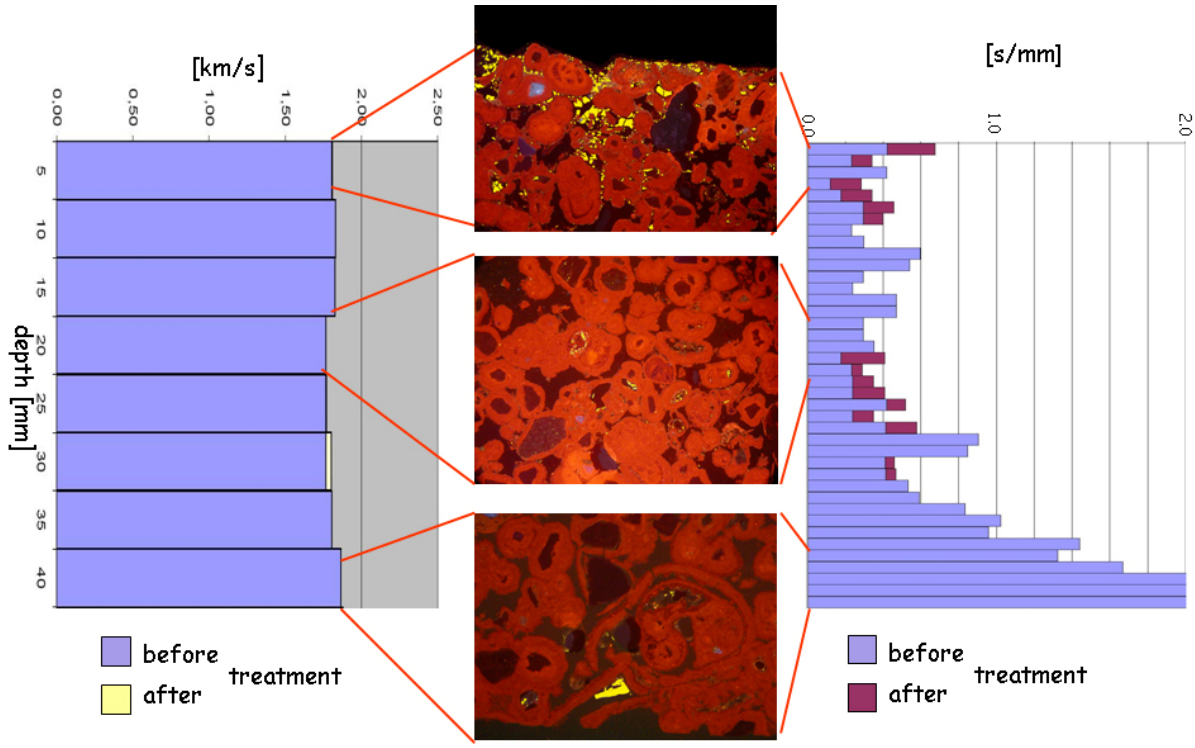

Fig. 13. Comparison of US (left) and DR (right) values with the CL observation of Sóskút Limestonein the function of depth (silica gel = yellow (bright) areas; pseudo colour image).

The increase of drill resistance in a depth of 25 to 30 mm suggest also the presence of the consolidant in that zone, however clear evidence for the precipitant was not found in this depth. Sharp changes in the drill force values may also refer to the inhomogeneous fabric of the stone (Fig. 13).
Ultrasound transmission velocity data of Eger Tuff showed a clear increase in all depths after the consolidation; however CL microscopy clearly proved a maximum penetration depth of 1 cm of the consolidant. Similar to US data DR values also show limited correlation to the optical observations (Fig. 14).

By means of cathodoluminescence microscopy, a relatively homogeneous distribution of the silica gel was proved in the Budafa Sandstone. Nevertheless the correlation between optical observation, US and drill resistance data was in this case also limited. Although increasing US values referred to the presence of consolidant in the pore space of the sandstone, the high amount of silica gel in the subsurface zones has not appeared in the ultrasonic values. Drill resistance values show in all depths a clear increase (Fig. 15).

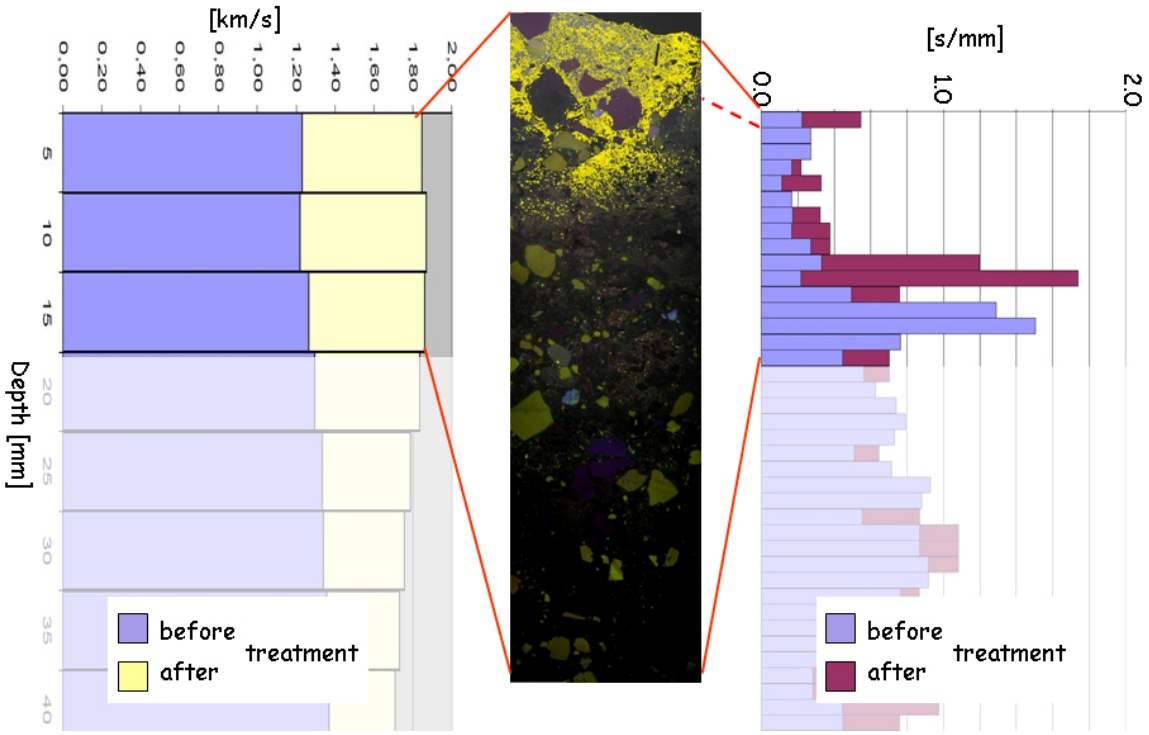

Fig 14. Comparison of US (left) and DR (right) values with the CL observation of Eger Tuff in the function of depth (silica gel = yellow (bright) areas; pseudo colour image).

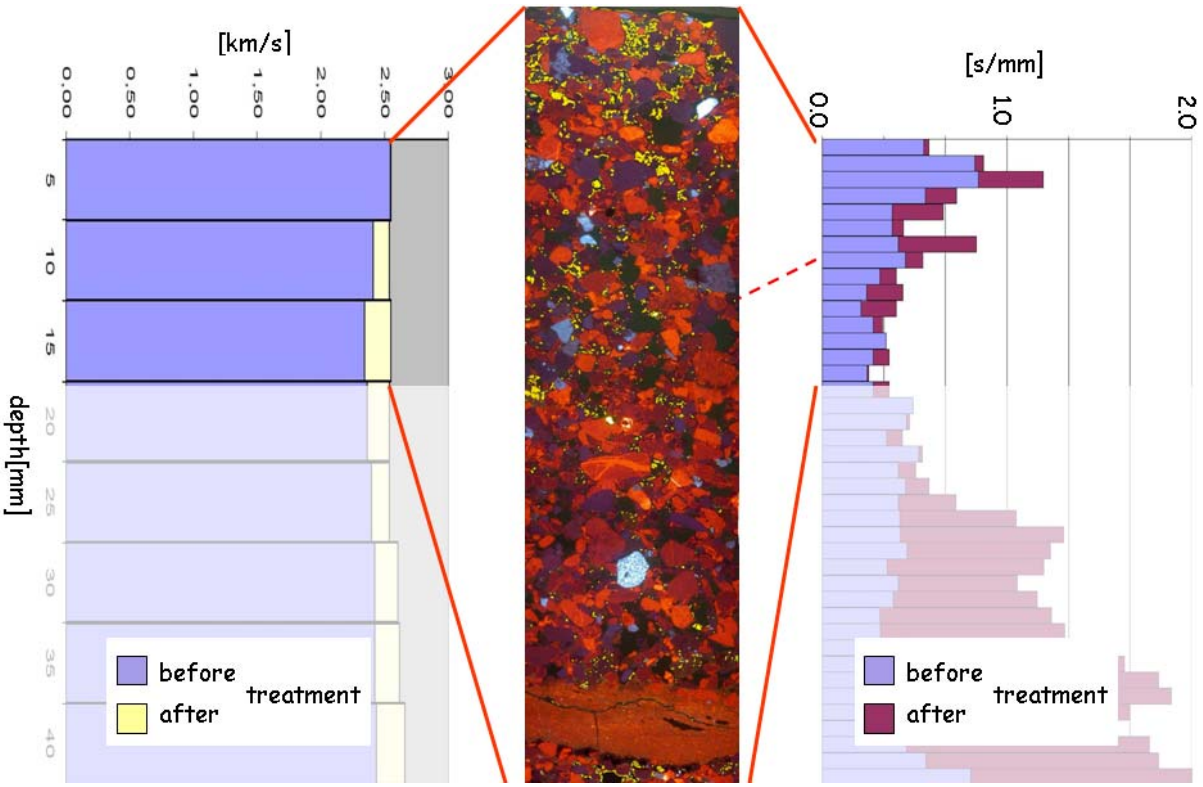

Fig 15. Comparison of US (left) and DR (right) values with the CL observation of Budafa Sandstone in the function of depth (silica gel = yellow (bright) areas; pseudo colour image).

5 DISCUSSION AND CONCLUSIONS

This study assessed the visualisation and performance of an ethyl silicate – Funcosil KSE 300 - consolidant in a porous oolitic limestone, a volcanic tuff, and a calcareous sandstone of different pore radii. Different microscopic techniques were used for the 2 and 3 dimensional visualisation of the precipitant. The results show that the combined use of polarizing, cathodoluminescence, and scanning electron microscopy in a range of different magnifications is a powerful method to detect the amount, distribution, shape, and size of solid silica gel consolidants in the pore space of a porous stone. Nevertheless, it must be noticed that, due to the optical properties of the amorphous gel, the polarising microscopy has only limited capacity of detection. Based on the CL microscopic and SEM observations, some important conclusions concerning the consolidant can be drawn.

Although the *in situ* observation immediately after the treatment showed a full penetration of the KSE in the Sóskút limestone, the results of the microscopic observation refer to an irregular distribution of larger gel fragments of a size of 20 to 100 μm. Such large gels can be found either directly below the surface or in irregularly distributed zones with pore radii smaller than 100 microns, or in intragranular, semi closed pores. The former phenomenon refers to the more intensive precipitation of the consolidants in the surface near zones that can also indicate a slight over-consolidation of the outer surface. The precipitation of irregularly distributed large gels seems to be controlled by the zones of smaller pore radii (cf. also Maravelaki-Kalaitzaki et al., 2008). Zones with large amount of microfossils and shell fragments often match the above criteria.

The SEM-SE/BSE observations showed that, besides the irregularly distributed large gel fragments, a homogenously distributed, approx. 1 to 5 microns thick silica gel coating covers the single carbonate grains. This corresponds with the in situ observation of the penetration depth after the vacuum treatment.

In accordance to the observations resulting from other investigations (Maravelaki-Kalaitzaki et al., 2008), also here the large gels and thin coatings are amorphous and show typical drying shrinkages. In most cases a poor bond to the carbonate cement could be detected. Evidence for "real" silica gel bridges between the adjacent ooid grains has not been found.

On the basis of CL observation some preliminary results can be drawn about the behaviour of consolidant in the Eger Tuff and Budafa Sandstone.

Due to the characteristic CL colour of the gel and the lack of the luminescence of volcanic glass the consolidant could be easily visualized in the pore space of the Eger Tuff. Its distribution was more homogenous than it was found in the Sóskút Limestone, however the observed maximum penetration depth was only 1 to 1.5 cm. The average size of gel fragments vary between 20 and 80 microns.

The consolidant observed by cathodoluminsecence microscopy in the Budafa Sandstone have similar features to those found in the Sóskút Limestone. In this stone type the consolidant was more homogenously distributed than in the porous limestone. Large amount of gel detected directly below the surface refers either to a slight over-consolidation of this zone and/or to the prompt precipitation due to the reaction of ethyl silicate with atmospheric water vapour.

Evidence for silica gel bridges between the adjacent mineral grains has not been found in the tuff and sandstone either.

In view of the above described observations concerning the places of precipitation, the thickness of consolidant layers on pore walls, the frequency of cracks, etc., there remains some doubt about the efficacy of the investigated treatments.

This hypothesis is also suggested by the comparison of ultrasound transmission velocity and drill resistance values. In most cases US data did not show any correlation with the optical observations, such as e.g. amount and place of precipitation, as well as penetration depth. This is partly probably due to the low resolution and/or sensibility of the technique. Drill resistance measurements showed some better results, however in most cases only limited correlation was found with the optical observations. Furthermore comparative analyses have proved that the increase of ultrasound transmission velocity and drill resistance values after the consolidation do not necessary refer to the efficacy of the treatment.

Based on the results it can be stated that the use of optical microscopy is a powerful method to obtain the distribution, penetration depth, size, shape, and binding capacities of an ethyl silicate consolidants in porous stones. Its combined use with ultrasonic transmission velocity and drill resistance measure-

ment may help to better understand the behaviour of this type of consolidants and to choose the appropriate product for individual tasks.

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