Mérnökgeológia-Kőzetmechanika 2008 (Szerk: Török Á. & Vásárhelyi B.) oldalszám: 177-184

Use of confocal laser scanning microscopy in the characterization of the void space of natural stones

Kovács Tímea
University of Oviedo, Department of Geology, Oviedo, Spain; timea@geol.uniovi.es

ÖSSZEFOGLALÁS: Természetes kőanyagok fizikai tulajdonságait jelentős mértékben befolyásolja pórusrendszerük jellege. A porozitás mértéke és a pórusok méreteloszlása mellett, az anyag fajlagos felülete, a pórusok és repedések geometriai tulajdonságai pl. alakja, konnektivitása, stb is fontos paraméterek. Ez utóbbi tulajdonságok vizsgálatára egyedül a mikroszkópos módszerek adnak lehetőséget, amelyek viszont a pórustér komplex, három-dimenziós rendszerét két-dimenziós formában képezik le, ezzel hibáknak adva esélyt. A konfokális pásztázó elektronmikroszkóp (Confocal Laser Scanning Microscopy – CLSM) legnagyobb előnye, hogy optikai metszetek készítésével lehetőséget ad 3D vizsgálódásra. A kutatás során a CLSM módszer alkalmasságát vizsgáltuk kis porozitású, kristályos kövek porozitásrendszerének tanulmányozására. A részletes, 3D megfigyelések mellet digitális képelemzéssel kvantitatív és összehasonlító méréseket is végeztünk más módszerekkel nyert mérésekhez képest, illetve különböző számú sókristályosítási ciklusnak alávetett mintákon. Eredményeink arra engedtek következtetni, hogy bár a CLSM kiválóan alkalmas a pórusrendszerek megfigyelésre és leírására, a vizsgált paraméterek mérése nagyban függ a mérési körülményektől, illetve, a módszer viszonylag alacsony felbontása jelentős adatvesztéssel járhat terményetes kőanyagok esetén.

ABSTRACT: The void space characteristics of porous materials – such as porosity, void size distribution, geometry, connectivity of voids, specific surface of the material etc. – have a strong influence on their physical properties. Some of these parameters can only be accurately investigated by means of direct, microscopy techniques. The Confocal Laser Scanning Microscopy (CLSM) is one of the few methods that provide the possibility of three dimensional imaging of the void space by means of serial optical sections and – completed with digital image processing – allow quantitative measurements, as well. In this work we investigated the use of CLSM for the characterisation of low porosity, crystalline natural stones and for the monitoring of the evolution of their void space during artificial weathering by means of salt crystallisation. Based on our experience, the CLSM is a suitable method for the observation and description of the void space of porous materials but the quantification is largely influenced by the measurement conditions and, because of the relatively low resolution, the microporosity of natural stones cannot be detected.Rövid, lényegre törő összefoglalás, maximálisan 15 sor terjedelemben.

Kulcsszavak: confocal laser scanning microscopy, crystalline stone, void space structure, salt crystallization

1 INTRODUCTION

The fact that the void space characteristics of porous materials have a strong influence on their physical (mechanical, hydraulic, thermal) properties is widely accepted. The most important ones of these characteristics are the open and closed porosity, void size and void size distribution, the geometry, connectivity and tortuosity of the voids and the specific surface of the material. In this research we take into consideration only those parameters that control the fluid transport properties, and so are crucial for the understanding of several geoscience and engineering issues, such as, deterioration of building stone materials, transport of salts and contaminants, displacement and storage of hydrocarbons etc.

Several techniques – direct and indirect ones – exist for the examination of the void space of solids. The most basic of the indirect ones are the hydraulic properties (water absorption, capillarity uptake, water vapour permeability etc), which give information about the water movement kinetics in the material. The gas adsorption and the mercury intrusion porosimetry are also widely used techniques pro-

viding data about the open porosity, pore size distribution and specific surface. However, important aspects, such as pore geometry and tortuosity etc. can only be examined by means of direct, microscopy techniques. These imaging methods must be completed with stereological measurements or digital image processing for quantification, but the fact that 2 dimensional images must be used for the determination of a 3 dimensional structure always carries some risk of misinterpretation (Friedrich et al., 1995; Friedrich, 1999). The confocal laser scanning microscopy (CLSM) provides the possibility of three dimensional observations by means of serial optical sections (Montoto et al., 1995) and in the past two decades it has become more and more popular in geoscience researches. It has been used to investigate radioactive waste disposal capacity of low porosity rocks (Montoto & Mateos, 2006), hydrocarbon reservoir potential of sandstones (Petford et al., 1999), development of thermal and mechanical cracking in granites (Menéndez et al., 1999) pore geometry of sandstones (Menéndez et al., 2001), fracture roughness of granites (Chae et al., 2003) etc.

In this work we have been investigating the use of CLSM for the characterisation of low porosity, crystalline natural stones and for the monitoring of the evolution of their void space during artificial weathering by means of salt crystallisation. The salt crystallization is a serious weathering agent causing many problems in monumental, as well as modern constructions, knowing the exact mechanisms and their effect on the void space of porous materials is an important issue. The main aim of this study was to evaluate the reliability of the CLSM method for the investigation of this question not only qualitatively, by observations, but also quantitatively and comparatively.

We used only crystalline stones in this research, because of the special void space structure of these materials. They have a void space structure of fissure type, - very different from that exhibited by cemented stones such as sandstones, limestones, etc. – and because of their typical features – low porosity values, channelled water pathways etc. – their characterization sometimes requires special methodologies.

2 PRINCIPLES OF THE METHOD

The original concept of the confocal microscopy was first developed by Marvin Minsky in the middle of the 1950s, but - due to the lack of intense light sources, necessary for the imaging and high capacity computers, necessary to handle the large amount of data – it didn't become a practically used method until the 1980s. Its common application started first in biological sciences.

The most important difference between the confocal and the traditional microscopies is the way of illumination and detection. Only a unique point of the sample is illuminated at a time by coherent light emitted by a laser system; and by inserting a pinhole – a confocal – in the way of the excited secondary fluorescence light only the signal of that point in the focal plain is detected by the photomultiplier; light from planes above and below that point is eliminated. The surface of the sample is scanned sequentially in the XY plane and, by means of a motorized stage, the vertical position of the sample can be controlled so two dimensional optical sections can be obtained in different depths. (Friedrich, 1999; Menéndez et al., 2001; Claxton et al., 2008)

The point to point detection manner and the use of laser light source both enhance the resolution of the CLSM, compared to other microscopy techniques, up to the degree that the lateral resolution exceeds the theoretical limit of the Raileigh criterion and can be calculated as:

$$F_{xy} = 0{,}4\lambda / NA \tag{1}$$

Where λ is the wavelength and NA the numerical aperture of the objective.

The vertical resolution is given by the half-width value in the z-direction as:

$$F_z = 1{,}28n\lambda / NA^2 \tag{2}$$

The n value is the refractive index of the matrix, which can be air or immersion oil (Onishi et al., 2005).

Of course, in the case of quantification by digital image processing the pixel resolution, which is usually smaller than the optical one, will determine the final resolution of the method.

During the image capturing the quality of the image can be improved by changing the offset and the gain settings. The first one can be used to decrease the background noise by adding a positive or negative voltage to the signal; and the second multiplies the output voltage by a constant factor so increasing the intensity without creating new grey levels (Claxton et al.,2008)

3 MATERIALS AND METHODOLOGY

The three crystalline stones selected for investigation are a marble, an andesite and a granite. They are stone types used for monumental purposes worldwide and they have local importance as monumental and ornamental stones, as well.

The Macael marble is a Late-Triassic carbonate rock that suffered poli-methamorphosis during the Alpine orogeny (Rodríguez-Gordillo & Sáez-Pérez, 2006) belonging to the Nevado-Filabride Complex in the Betic Internal Zone in Southern-Spain. It is a pure white (sometimes with greyish layers), heterogranular marble with an average grain size of 700-500 μm. Due to the orientation of the calcite grains and the intercalations of layers richer in mica, pyrite, quartz and feldspar grains, it has a slight anisotropy. Its open porosity is around 0,5%, which is composed by fissures of very small length and aperture (< 1 μm) and low tortuosity.

The Silvestre Porrisal granite is a two-mica leucogranite with hypidiomorphic granular texture, which belongs to a Variscan granite batolite in the Galicia-Tras-os-Montes zone within the Central Iberian Zone in North-Western Spain (Bustillo-Revuelta, 1996). Its average grain size is about 1 mm but the grain size distribution is very wide varying from the centimetre to the sub-millimetre scale. It has a high, fissure-type porosity (open porosity: around 4%, low tortuosity) and because of the orientation of the fissures it is highly anisotropic as well.

The Szobi andesite – a microporphyritic quartz-andezite – belongs to the volcanic complex of the Börzsöny and Visegrád Mountains of North-Hungary. It was formed during the calc-alkaline volcanism of the Carpathian volcanic arc taken place from the Miocene to the Quarternary (Harangi et al., 2001). The average grain size of phenoclasts is 1-2 mm and of matrix is 50μm; its open porosity is around 4%; the fissures have small apertures (≤1 μm) but very high tortuosity. The stone is isotropic.

The semi-quantitative mineralogical composition, the value of the open porosity and the coefficients of anisotropy for each stone are shown in the table 1.

	Mineralogical composition (%)								open porosity (%)	coefficient of anisotropy
	calc	musc	bio	Q	plg	mic	magn +pyr	matrix (%)		
marble	90	tr	-	tr	tr	-	-	-	0,4	1,1
granite	-	20	5	30	25	20	-	-	4,4	1,4
andesite	-	-	10	tr	30	-	7	50	4,6	1,0

Table 1. The semi-quantitative mineralogical composition, the value of the open porosity and the coefficients of anisotropy (based on the velocity of ultrasound propagation) of the three stones. calc=calcite; musc=muscovite, bio=biotite; Q=quartz; plg=plagioclase; mic=microcline; magn=magnetite; pyr=pyrite; tr=traces.

The first step of the research was the characterisation of the void space properties of the three stones types by means of CLSM. The sample preparation for this purpose starts with the impregnation of the specimens with a resin containing fluorescein dye. We used Rhodamine D, which is frequently used for this purpose. Its emitted light wavelength is λ=514 nm. The impregnation happens under vacuum first, and then under hydrostatic pressure of 10MPa. For the cutting of the samples a low deformation cutting machine is used to avoid the creation of artefacts during the preparation. Finally polished thin sections of 150-200 μm thickness are prepared with a surface of approximately 6 cm^2. For each stone two samples were taken for the characterization. From each sample 3 thin sections were prepared in the x, y and z directions in respect to the original position in the quarry and the directions of anisotropy, when there is any. The technical parameters of the microscopy method are described separately in the next section.

We used mercury porosimetry data for comparison, as similar parameters can be measured by the two techniques, although via very different processes. The Hg intrusion porosimetry was carried out on a Micromeritics AuroPore III type porosimeter and 4-4 cylindrical samples of 2,5 cm height and approximately 2 cm diameter were used for this measurement for each stone.

The second step was the monitoring of the evaluation of the void space of the stones as a response for artificial weathering. For this purpose we selected the salt crystallisation test following the European standard, UNE-EN 12370, as salt crystallisation is one of the most serious weathering agents, it is present under several environmental and climatic conditions and its effect largely depends on the void space of the materials. The samples were examined after 25 and after 45 cycles. For each stone two samples were taken for analysis at the different stages of the ageing test. The sample preparation happened the same way as for the characterization.

4 TECHNICAL ASPECTS – MEASUREMENT CONDITIONS

The instrument used in this study was a Leica TCS-SP2-AOBS type microscope equipped with a multilaser configuration, of which we used a Diode Laser (405 nm) for the marble and the andesite and a Helium-Neon Laser (543 nm) for the granite. The detected wavelength was within the range of 419-513 nm in the first case and in the 560-635 nm in the second. The used objectives were a PL APO 10X/0.40, a PL APO 20X/0.70 multi-immersion, a PL APO 40X/1.25-0.75 oil immersion and a PL APO 63X/1.40 oil immersion objective. The images have 1024x1024 pixel size. From each point of measurement a series of images were taken in different depths. The thickness of this optical sectioning depends mostly on the absorption spectrum of the rock forming minerals (Menéndez et al. 2001). In our case the average depth of penetration was around 60 μm for the granite, around 25 μm for the marble and around 15 μm for the andesite. The number of sections in the series depended on the thickness, usually keeping a 1-3 μm disctance between the images.

For the digital image processing the Leica QWIN software was used on a Leica Q550 QUANTIMET system with a Intel Pentium III (800 MHz) processor, 768 MB RAM memory, 40 Gb hard disk and a Matrox Milenium 32 MB graphic card. The software is complemented with some extra functions to suite the special purposes we needed (Martínez-Nistal, 1993).

To evaluate the influence of the microscope and software settings on the quantification, we carried out some preliminary measurements on one area of a granite sample with different objectives and different gain settings. The photos were taken using the 10x, 20x, 40x and 63x objectives and on two gain values: 330 and 420. The images are shown in figure 1. and the corresponding results, which are the values of the parameters of the single image, in table 2.

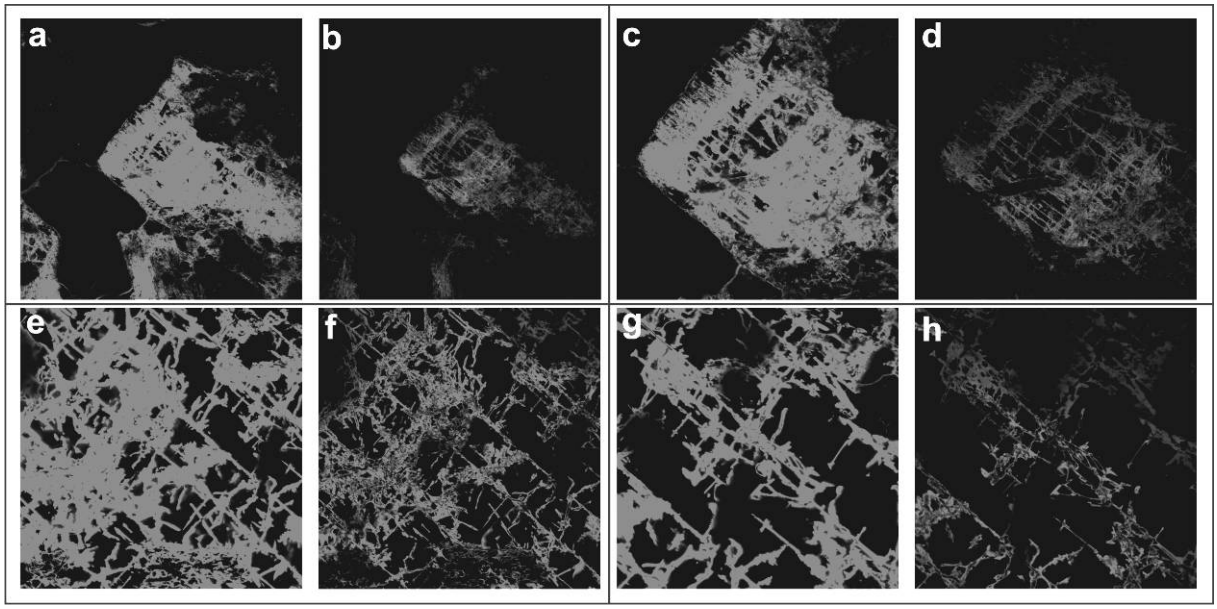

Figure 1. *Microphotographs taken by 10x (a, b); 20x (c,d); 40x (e,f) and 63x (g,h) objectives and by different gain settings: 420 (a, c, e, g) and 330 (b, d, f, h).*

objective	porosity (%)		specific surface (μm^{-1})		average void size (μm)		maximum void size (μm)	
	gain= 330	gain= 420	gain= 330	gain= 420	gain= 330	gain= 420	gain= 330	gain= 420
10x	6,6	24,5	0,013	0,020	18,5	39,8	84,7	189,8
20x	12,5	36,4	0,053	0,058	8,0	18,4	30,7	105,1
40x	28,4	55,0	0,207	0,158	3,9	8,4	17,6	48,3
63x	14,7	33,3	0,176	0,188	2,4	4,3	8,7	20,7

Table 2. *Results of the quantification of the images of fig.2. by digital image processing.*

As we can see, the porosity and the specific surface values are the highest when using the 40x objective and the void size parameters increase with the decreasing magnification. This direct correlation between the measured void sizes and the magnification of the objective shows the importance of the resolution for the quantification. The gain setting also has a great influence on the measurements. In images especially with low magnification we can observe how the smaller pores close to each other seem to fuse when the gain is higher so they will be measured as one larger void. This will increase the

void size and the open porosity values, as it is proved here: the measurements taken with gain 420 are significantly higher than those with gain 330. The influence of the magnification on the values is the same with both gain settings.

Taking into consideration the above listed aspects we decided to use the 40x objective, which gives the highest values so probably the most information for all the images taken for quantification; but a lower and constant gain setting to avoid the mistakes of the imaging. Evidently the gain and offset settings largely depend on the material: we aimed at getting the highest amount of information without changing the actual values in all the cases.

5 RESULTS

In figure 2. three dimensional reconstructions of the void space of each stone type are shown. These images were built by superimposing a series of images taken of a given area of the samples in different depths.

The void space of the granite is composed by trans- and intergranular macro fissures (fig.2.a) and intragranular voids (both fissures and pores) mostly in the feldspar grains. The macro fissures are well connected, are usually not tortuous and have a preferential orientation perpendicular to the xy plane, which is the horizontal plane of the quarry; but there are more than one fissure groups. The ramifications and junctions of the fractures in different depths can be observed very well. The other type of porosity due to feldspar weathering has significantly smaller aperture. These voids sometimes follow the crystalline structure of the feldspars or are disoriented. With low magnification the highly weathered minerals appear as colored blurs and can significantly influence the values of the quantification. The marble mostly contains intergranular fissures of small aperture among the calcite grains (figure2.b), and some intragranular pores can be observed, as well, connected to the mica and feldspar inclusions. Due to the relatively large grain size of the calcites and the relatively low penetration depth, the 3D imaging of these intergranular fissures is less effective. The pores connected to feldspar and muscovite crystals are usually observed as small spots – spherical pores -; due to their small size more detailed observations are not possible. The andesite has a very different void space compared to the two other stones. Here most of the voids have so small apertures that even with the highest magnification (63x objective) they appear like small, colored spots but no closer observation can be carried out. Most of these voids are situated in the fine grained matrix but the biotite and feldspar phenoclasts also show the signs of weathering. The few larger fissures are either connected to the phenoclasts, like the one on figure 2.c., which is a grain boundary fissure around a feldspar grain, or they are in the matrix, in which case their tortuosity is extremely high.

For the quantification of the void space parameters we used 150 images for the marble and the andesite and 250 for the granite, where the coarser grain size requires a larger statistical population to get reliable values.

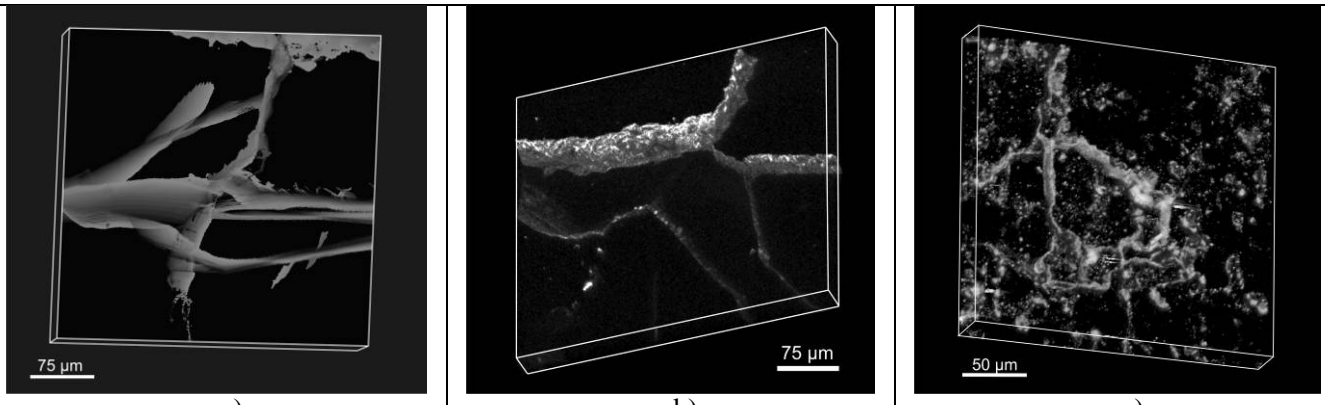

Figure 2. *Three dimensional reconstructions of the void space of the Silvestre Porrisal granite (a), the Macael marble (b) and the Szob andesite (c).*

Table 3. shows the open porosity, specific surface and average void size values measured by confocal laser scanning microscopy before the salt crystallization test (0 cycles), after 25 and after 45 cycles. Other fractographic parameters, such as connectivity, orientation of fissures and fractal dimension can also be quantified by this method but these parameters are not discussed in this paper. As the measured values did not show significant differences in different orientations they are all discussed together.

		0 cycles			25 cycles			45 cycles			0 cycles (Hg porosimetry)		
		porosity (%)	specific surface (m^2/g)	average void size (μm)	porosity (%)	specific surface (m^2/g)	average void size (μm)	porosity (%)	specific surface (m^2/g)	average void size (μm)	porosity (%)	specific surface (m^2/g)	average void size (μm)
granite	aver.	2,4	0,011	2,8	2,9	0,011	3,0	3,6	0,013	3,0	3,3	1,01	0,025
	st.dev.	4,5	0,014	1,0	4,8	0,017	1,5	5,4	0,019	1,4	0,1	0,02	0,0015
marble	aver.	0,2	0,001	2,0	0,6	0,003	2,5	0,7	0,004	3,5	0,97	0,51	0,014
	st.dev.	0,3	0,001	2,3	0,5	0,002	0,9	1,2	0,002	1,7	0,11	0,03	0,0020
andesite	aver.	0,3	0,001	3,0	0,1	0,001	2,1	0,2	0,001	2,6	3,5	3,32	0,008
	st.dev.	0,5	0,002	1,2	0,4	0,002	1,1	0,5	0,003	1,9	0,1	0,07	0,0001

Table 3. Pore space parameters of the three stones measured by CLSM-DIP after 0, 25 and 45 cycles of salt crystallization test and by Hg porosimetry before the test.

As we can see in the first column of table 3., the original open porosity values measured for the marble and the andesite are very similar: 0,2% and 0,3%, respectively, while it is an order of magnitude higher (2,4%) for the granite. The average void size values are practically identical for the three stones, around 2-3 μm. And finally, the specific surface values are surprisingly low, being 0,001 m^2/g for the marble and the andesite and 0,01 m^2/g in the case of the granite.

As the standard deviations are quite high, for the evaluation of the changes during the ageing tests we preferred to take into account the tendencies only, and not to quantify numerically these changes. The open porosity values increase after 25 and 45 cycles of the salt crystallization test for the granite and the marble, but in the case of the andesite the values do not show any consequent tendencies. The specific surface, as well as the average void size, increases for the marble while in the other two cases the changes are not really significant (granite) or the tendencies are not clear (andesite).

6 DISCUSSION

Our first aim was the visualization and the 3D imaging of the void space of the materials. The method proved to be ideal for this purpose in the case of the Silvestre Porrisal granite, where the high fissure density and the wide apertures allow a detailed and reliable observation. In the case of the Macael marble the method was still quite useful. The intergranular fissures, which follow the grain boundaries of the calcite crystals, can be observed well; although, for the construction of a real 3D void structure, deeper penetration would be necessary because of the grain size of this marble. For marbles with smaller grain size the technique may be more suitable. On the other hand the Szob andesite could not be reliably investigated with this method due to the very small void apertures and the low penetration of the laser. In this case we had to accept that the majority of the voids are under the detection limit of the microscope and even for those which are detected; the detailed observation or the 3D imaging may be more complicated.

To evaluate the reliability of the quantification of the void space parameters we compared the measured values to measurements taken by Hg porosimetry. In table 3. the results of the characterization by CLSM are shown in the first column and those by Hg porosimetry in the last one. If we compare them to each other we will find surprisingly high differences. All the porosity values measured by CLSM are significantly lower than those measured by Hg porosimetry but the highest difference occur in the case of the andesite, when there is an order of magnitude difference between the two numbers. For the other parameters the deviations are even more significant: the average void size values being two orders of magnitude higher when measured by microscopy and the specific surface values being two or in the case of the andesite three orders of magnitude lower measured by microscopy. The differences in the open porosity values can be explained by the range of detection of the method. As for the CLSM the lowest detection limit is about 1 μm evidently we lose quite a lot of information, especially in the case of the andesite, where – based on measurements by other methods – 80% of the voids has a

diameter lower than 1 μm. But the fact that we detected almost identical average void sizes for all the three stones is a defect of the method. This phenomenon is the most evident if we compare the void sizes of the granite and the andesite: both the Hg porosimetry measurements and the visual observations prove clearly that the granite has a significantly higher average void size than the andesite, but the quantification by CLSM gave the opposite result. This error is due to the optical resolution of the analyzed images, which is not high enough to give reliable information about the sizes; and it also suggests that the real average value is equal or smaller than the measured one for all the three stones, which fact is proved by the porosimetry. For the very low specific surface values both of the above mentioned aspects can be responsible, especially that the specific surface of a material is mostly connected to its microporosity – lower the void size higher the specific surface – and that is exactly the void range that remains undetected by the microscope. But we also have to keep in mind that the two methods measure this parameter in a very different way: the digital image analysis calculates the length of the borders of a profile as a function of a reference surface (the surface of the image) and gives the final value as μm^{-1}, which we have to convert to m^2/g to make it comparable to the value measured by the porosimetry. This conversion may give rise to some doubts, although the measured parameter is the same in both cases, so they should be comparable.

These striking differences suggest that the CLSM method – although ideal for the observation of the porous space – is not always reliable for quantification, especially if materials with higher proportion of small voids are concerned. Still, if we carry out the measurements – from the sample preparation till the image processing – in the same way, the method could be useful for comparison; always keeping in mind that we are monitoring only a part of the open voids.

The changes due to the salt crystallization weathering were also monitored with other methods (Hg porosimetry, hydraulic properties) as well, which are not discussed in this paper. Based on these other observations we expected an increase in the open porosity and the specific surface values. In the case of the open porosity of the marble and the granite these preliminary expectations were confirmed, but not for the andesite and not for the specific surface parameter. This supports our former suspicion that the method is not reliable for measurements of properties determined by smaller voids, not even for comparison. On the other hand the fact that it worked for the monitoring of the open porosity of the granite and the marble proves that for materials with larger void size it is a suitable method.

There is one more weak point of the method, which is the impregnation of the samples with the flourescein resin. Although it is carried under vacuum first and under high pressure in the second step we never can be perfectly sure if the resin reached all the open voids. The evaluation of this needs further investigation by means of scanning electron microscopy.

7 CONCLUSIONS

Three different crystalline stones were investigated in this research by means of CLSM. Besides the visual observation of the void space of the materials, quantitative evaluation of their most important parameters were carried out and were compared to results gained by Hg porosimetry. The evaluation of the same parameters was monitored during 45 cycles of salt crystallization test.

The conclusions withdrawn from the investigation are the followings:

- The confocal laser scanning microscopy is a suitable method for the three dimensional observation of the void space of porous materials. It is a unique technique for the investigation of the geometric features of pores and fractures.
- The quantification of the open porosity is quite reliable, but as the lowest detection limit is around 1 μm, it is recommended to use it together with other methods when the presence of smaller voids is probable.
- The sample preparation, the settings of the microscope, the magnification of the objective and the pixel resolution of the image processing can significantly influence the results of the quantification. Therefore, the method may be reliable for comparison of values measured under the same conditions, but the absolute values must be handled with care.
- Parameters determined by microporosity can be seriously misinterpreted.
- The increase of the open porosity of the materials was observed due to the salt crystallization test, but the possible other changes were not detectable by this method.

ACKNOWLEDGEMENT

I would like to thank Angel Martínez Nistal and Marta Alonso Guervós from the Servicio de Proceso de Imágenes of the University of Oviedo for their technical support and my supervisors Rosa Maria Esbert and Modesto Montoto from the Departement of Geology, University of Oviedo for all their help. The research was funded by the Marie Curie Action EPISCON– Europen Phd in Science for Conservation – project.

BIBLIOGRAPHY

Bustillo Revuelta M., (1996): Potencial geológico de granitos en España, *Manual de Rocas Ornamentales*, (ed. J. Carlos López), Madrid, pp. 1-696

Chae B.G., Ichikawa Y., Jeong G.C., Seo Y.S., Kim B.C. (2003) : Roughness measurement of rock discontinuities using a confocal laser scanning microscope and the Fourier spectral analysis, *Engineering Geology* **72**: 181-199

Claxton N.S., Fellers T.J., Davidson M.W. (net access 2008.oct.): Laser Scanning Confocal Microscopy, http://www.olympusconfocal.com/theory/LSCMIntro.pdf

Friedrich J.T., Menéndez B., Wong T.F. (1995): Imaging the pore structure of geomaterials, *Science* **268**: 276-297

Friedrich J.T. (1999): 3D imaging of porous media using laser scanning confocal microscopy with application to microscale transport processes, *Physics and Chemistry of the Earth* **24** (7): 551-561

Harangi Sz., Downes H., Kósa L., Szabó Cs., Thrilwall M.F., Mason P.R.D., Mattey D. (2001): Almandine Garnet in Calc-alkaline Volcanic Rocks of the Northern Pannonian Basin (Eastern-Central Europe): Geochemistry, Petrogenesis and Geodynamic Implications, *Journal of Petrology* **42** (10): 1813-1843

Martínez-Nistal A. (1993): Discriminación, cuantificación y cartografiado de componentes petrográficos mediante proceso digital de multi-imágenes microscópicas, *Tesis doctoral, Facultad de Geología, Universidad de Oviedo* (Oviedo, Spain)

Menéndez B., David C., Darot M. (1999): A study of the crack network in thermally and mechanically cracked granite samples using confocal laser scanning microscopy, *Physics and Chemistry of the Earth* **24** (7): 627-632

Menéndez B., David C., Nistal A. (2001) : Confocal laser scanning microscopy applied to the study of pore and crack networks in rocks, *Computers Geosciences* **27**: 1101-1109

Montoto M., Martínez-Nistal A., Rodríguez-Rey A., Fernández-Merayo N., Soriano P. (1995): Microfractography of granitic rocks under confocal scanning laser microscopy, *Journal of Microscopy* **177**:138-149.

Montoto M., Mateos F. (2006): Characterization of water pathways in low permeable rocks at the rock matrix scale: Methodological review, *Journal of Iberian Geology* **32** (2): 197-213

Onishi C.T., Shimizu I. (2005): Microcrack networks in granite affected by a fault zone: Visualization by confocal laser scanning microscopy, *J. of Structural Geology* **27**: 2268-2280

Petford N., Davidson G., Miller J.A. (1999): Pore structure determination using confocal laser scanning microscopy, *Physics and Chemistry of the Earth* **24**(7):. 563-567

Rodríguez-Gordillo J., Sáez-Pérez M.P. (2006): Effects of thermal changes on Macael marble: Experimental study, *Construction and Building Materials* **20**: 355-365.