COBISS: 1.01

FIRST STEPS IN LIMESTONE WEATHERING AND EROSION: AN ATOMIC FORCE MICROSCOPY (AFM) AND SCANNING ELECTRON MICROSCOPY (SEM) APPROACH

UPORABA MIKROSKOPA NA ATOMSKO SILO (AFM) IN VRSTIČNEGA ELEKTRONSKEGA MIKROSKOPA (SEM) PRI ŠTUDIJI ZGODNJE FAZE RAZTAPLJANJA APNENCA

Joan J. FORNÓS[1], Lluís GÓMEZ-PUJOL[1,2], Joan CIFRE[3] & Ferran HIERRO[3]

Abstract UDC 551.311.2:552.541

Joan J. Fornós, Lluís Gómez-Pujol, Joan Cifre & Ferran Hierro: First Steps in Limestone Weathering and Erosion: An Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) approach

A combined atomic force microscope (AFM) and scanning electron microscope (SEM) experiment examining the first steps in limestone weathering and erosion is presented. The experiment deals with the exposure of polished limestone rock tablets to a Western Mediterranean coastal environment and with the rate and patterns of weathering addressed by roughness quantification and qualitative assessment of nanoforms. Observations show how rock surface roughness increases at high rates after four and six months of exposure, passing from initial roughness *RMS* values between 14 and 32 μm to values between 396 to 492 μm. From the qualitative SEM approach, it can be concluded that the roughness increase relates with the widening of the space between rock grains and results in the isolation and detaching of rock grains.

Keywords: limestone weathering, AFM, SEM, roughness.

Izvleček UDK 551.311.2:552.541

Joan J. Fornós, Lluís Gómez-Pujol, Joan Cifre & Ferran Hierro: Uporaba mikroskopa na atomsko silo (AFM) in vrstičnega elektronskega mikroskopa (SEM) pri študiji zgodnje faze raztapljanja apnenca

V članku predstavimo uporabo mikroskopa na atomsko silo (AFM) in vrstičnega elektronskega mikroskopa (SEM) pri študiji zgodnjih faz raztapljanja apnenca. Na zglajenih apnenčastih ploščicah, ki smo jih izpostavili kemičnemu preperevanju v obalnem okolju zahodnega Sredozemlja, smo opazovali hitrost raztapljanja ter vzorce in oblike, ki pri tem nastajajo. Rezultati kažejo, da se hrapavost najbolj poveča v štirih do šestih mesecih, in sicer koren srednjega kvadrata (RMS) hrapavosti zraste od začetnih 14 do 32 μm, do končnih 396 do 492 μm. Na osnovi kvalitativnih SEM analiz sklepamo, da je razvoj hrapavosti povezan s širjenjem medzrnskega prostora in odnašanjem zrn.

Ključne besede: preperevanje apnenca, AFM, SEM, hrapavost.

[1] Karst and Littoral Geomorphology Research Group, Universitat de les IllesBalears, Ctra. Valldemossa km 7.5, 07122 Palma, IllesBalears, Spain, e-mail: joan.fornos@uib.es

[2] Mediterranean Institute for Advanced Studies, IMEDEA (CSIC-UIB), Miquel Marquès 21, 07190 Esporles, IllesBalears, Spain, e-mail: lgomez-pujol@uib.es

[3] Universitat de les IllesBalears, Ctra. Valldemossa km 7.5, 07122 Palma, IllesBalears, Spain, e-mails: joan.cifre@uib.es, ferran.hierro@uib.es

Received/Prejeto: 22.09.2010

INTRODUCTION

Limestone weathering and erosion result in a large variety of karren forms that have been a fascinating object of interest for geomorphologists. Nowadays, there are several methods and principles used to estimate dissolution rates in karst areas (Gabrovšek 2009), but these approaches are not of high enough resolution to explain the development of a large set of karren forms (Viles 2001). Despite of the large number of observations and descriptions developed on karren features (i.e. Ginés *et al.* 2009), specific knowledge of the physical, chemical and biological processes of their formation –mainly driven by dissolution– is scarce (Dreybrodt & Kaufman 2007; Fiol *et al.* 1997; Viles 1987). Nevertheless, several recent investigations have explored the response of calcite crystals to the chemistry of different aqueous solutions by means of Atomic Force Microscopy (AFM) (Gaebel *et al.* 2009; Hillner *et al.* 1992; Stipp *et al.* 1994; Rachlinf *et al.* 1993; Ruiz-Agudo *et al.* 2009). In fact, AFM opens a wide array of possibilities that are quite different from chemical and crystallography studies. Because AFM provides a basis for quantifying and analysing the distribution of surface height of a sample –at nm-μm scale– it can contribute to the characterisation of the first steps of limestone weathering from the rock surface properties and their evolution by means of roughness indices, a field where most of the contributions are related to a conceptual or a black box schema (Gómez-Pujol *et al.* 2007).

The present contribution provides a preliminary report on the experimental results of a one-year rock tablet exposure experiment. In this paper, we focus on rock surface roughness evolution on bare rock surfaces exposed to the atmosphere, and on the role that rock texture plays in the first steps of limestone weathering by using a combination of Atomic Force Microscopy (AFM) and Scanning Electron Microscope (SEM).

MATERIALS AND METHODS

The rationale of the experiment consists on exposing four similar fresh and flat limestone rock tablets to a coastal temperate environment under natural conditions for 1 year (10th October 2008 to 21st September 2009). Limestone rock tablets (~25 mm on each side and 5 mm thick) were prepared from a pre-cleaned and smoothed sample (polished to 0.05 μm) belonging to the Mesozoic (Cretaceous) folded limestones cropping out in the northeastern coast of Mallorca (Punta des Faralló). The rock is characterized by a mudstone texture and by abundant fracture planes and joints. Nevertheless it is a hard rock, with a Schmidt Hammer rebound value of 59.8. The composition is mainly calcite (91.4%) and dolomite (8.6%) and rock porosity is 6.6%.

Prepared tablets were attached in a horizontal position to a platform on the terrace roof of a coastal building in Es Barcarès (NW Mallorca) and exposed subaerially. Previously, each rock tablet was characterised quantitatively in terms of micro-roughness through AFM, and qualitatively by means of SEM in order to appreciate the attributes of rock cement and grains. These observations are referred to in the text as 'control' samples. The tablets were removed from the field after three, six, nine and twelve months of exposure (respectively December 2008, March, June and September 2009). Each of the retrieved tablets were subjected to both AFM and SEM study; these tablets are referred to as 'exposed' samples.

Atomic Force Microscopy (AFM) is a three-dimensional imaging methodology that is used increasingly in biological and crystallography research. It performs imaging and structure measurements from atomic to micron scale based on physical forces between the sample and the cantilever. The cantilever is a fine 'tip' or stylus of various hard materials that is connected to an electronic device that senses its movements as this is swept over the sample and measures depths and heights of the material beneath. From each of the exposed and control rock tablets, five random AFM images (10x10 μm) were obtained using a Nanoscope microscope (Veeco Metrology Group) equipped with an E scanner and a Nanoscope IV controller. Control tablet images were obtained in 'tapping mode' and exposed tablet images in 'contact mode', using phosphorous-dipped silicon cantilever with a nominal spring constant ranging between 20 to 80 N m^{-1} and nominal resonant frequency of 300 kHz. For rock or hard samples, attending to the analysis scale, there are no significant differences between tapping and contact method, although it is recommended to use the contact method for rough samples (DIVMG, 2001). Image data analysis was performed using the Scanning Probe Image Processor software (NanoScope™ Digital Instruments Veeco Metrology Group), which allows the computation of different roughness indices. Additionally, each tablet was explored using Scanning Electron Microscopy to in-

Tab.1: Roughness parameters used in this study.

Parameter	*Description*	*Measure*
RMS or R_q	Root mean square of height deviation taken from the image mean data plane.	$RMS = R_q = \sqrt{\frac{\Sigma z_i^2}{n}}$ where z_i is the relative height value at and i position, and n is the number of points within the image grid. Because plane tilt can introduce distortion in this parameter computation, all rock tablets where flat being the upper surface parallel to the miscroscope base plate. Additionally the same plane fitting and flattening was applied to all the samples in order to compare results. RGH_{RMS} is understood as a measure of the roughness degree of rock surface and of their spatial (i.e. sampled surface extent) (Gómez-Pujol 2001; McCarroll & Nesje, 1997).
R_a	Mean roughness index is the arithmetic average of the absolute values of the surface height deviations measured from the image.	$R_a = \frac{1}{n}\sum_{i=1}^{n}\left\|z_i\right\|$
K	Surface height kurtosis indicates whether data are arranged to flatly or sharply about the mean.	$K = \frac{1}{R_q^4}\frac{1}{n}\sum_{i=1}^{n} z_i^4$ where z_i is the relative height value at and i position, R_q is the root mean square of height deviations and n is the number of points within the image grid.
Sk	Surface height skewness represents the symmetry of surface data about a mean data values.	$Sk = \frac{1}{R_q^3}\frac{1}{n}\sum_{i=1}^{n} Z_i^3$ where z_i is the relative height value at and i position, R_q is the root mean square of height deviations and n is the number of points within the image grid. Skewness is a non-dimensional quantity, which is typically evaluated in terms of positive or negative. Where *Sk* is zero, an even distribution of data around the mean plane is suggested; where *Sk* departs largely from zero, an asymmetric one-tailed distribution is suggested, such as flat plant having a small sharp spike (>0) or a small deep pit (<0).
R_z	The *10 points mean roughness* is the average difference in height between the five highest peaks and the five lowest valleys relative to surface mean plane.	

dentify weathering nanoforms (Viles & Moses 1996) and also to obtain qualitative information on the weathering patterns and processes.

Roughness indices have been used as a measure of the degree of weathering due to different environments and processes and at different scales (Crowther 1997; Evans 1994; Gómez-Pujol *et al.* 2006; McCarroll 1992; Swantesson *et al*. 1992). McCarroll and Nesje (1996) review different roughness indices and techniques and suggest that the most appropriate indicator of both the roughness scale and magnitude is the standard deviation of the differences between the height values of a range of set horizontal intervals along the profile. We use different roughness indices according to the output possibilities of AFM in this study. From AFM images obtained, different roughness parameters were calculated, such as the root mean square average of height deviation or the mean roughness index, among others (Tab. 1). In that sense, roughness evolution is interpreted as a weathering indicator and for this issue, roughness increase and weathering are used as equivalent terms in results and discussion. Additionally, AFM tools allow us to obtain the integral of the surface height histograms of the surface above a reference plane as a function of the depth of that plane below the highest point in the image. This histogram, at a large scale, is equivalent to the hypsometric curve and its temporal evolution and can help to address where the main changes in rock surface occur.

The topsurface of each tablet was characterized by means of Scanning Electron Miscroscope (SEM) using a Hitachi S-3400N Type II SEM microscope. Samples were viewed uncoated under low vacuum to asses the general characteristics of rock tablet surface, roughness, and the presence of nanoforms (Viles & Moses 1998) recorded as a presence/absence ratio. SEM backscattered images were also used to estimate the rock tablet grain size by digital imaging processes using the IMAGE_J free software.

Meteorological parameters were monitored during all the exposition period by means of the two nearest meteorological stations (Pollença and s'Albufera) from the *Meteoclimatic* net.

RESULTS AND DISCUSSION

Table 2 shows the tablet surface roughness by the number of months of exposure.The roughness indices from each rock sample increases with exposure time. For instance, RMS or R_q values for exposed samples are at least twenty times larger than the same parameter values for control samples (Fig. 1). The rock surface roughness increases drastically during the first four months of exposure, with values increasing from an averaged RMS mean of 14 μm at placement to 396 μm at the fourth month. The roughness increases at lower rates in the following months, achieving RMS values around 425 μm after six and nine months of exposure, and close to 500 μm at the end of twelve months under the action of weathering agents. Taking into account that much of this change is related to the initial conditions of the polished surface (roughness increase rate of 2,700%), the exposed rock samples

Tab. 2: *Roughness parameters.*

Sample and exposure time		R_q (nm)	R_a (nm)	R_z (μm)	Sk	K
RT 1 # 3 months	C	14,38	9,85	0,13	-2,07	17,39
	E	*395,96*	*320,62*	*2,80*	*-0.08*	2,80
RT 2 # 6 months	C	28,41	18,99	0,25	-1,27	12,49
	E	*426,44*	*345,09*	*2,99*	*0*	*2,99*
RT 3 # 9 months	C	33,55	23,12	0,20	-0,88	6,12
	E	*423,17*	*339,30*	*2,86*	*0,05*	*2,86*
RT 4 # 12 months	C	27,47	18	0,22	-013	10,19
	E	*491,53*	*305,01*	*1,99*	*-0,30*	*3,41*

C: control sample; E: exposed sample

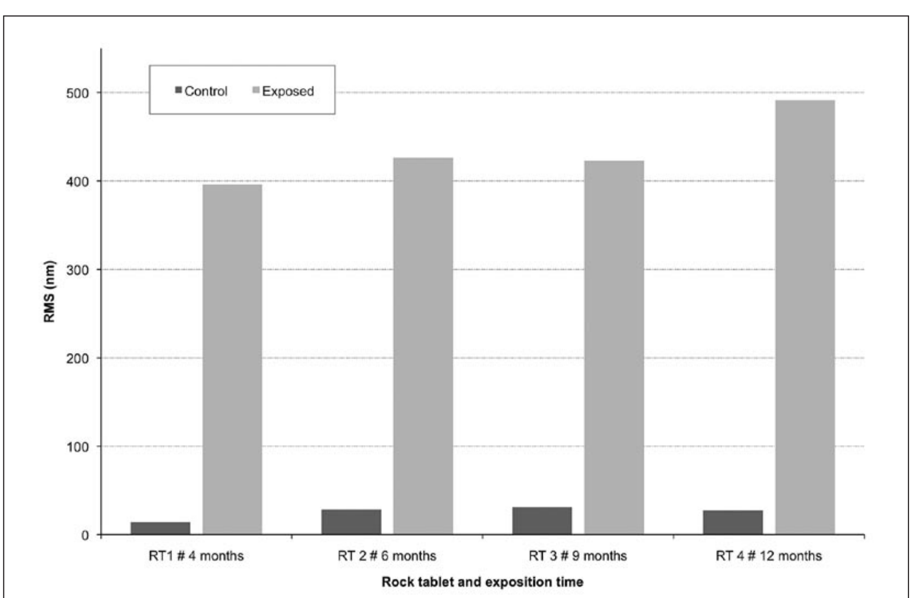

Fig. 1: Rock tablet surface roughness evolution during the exposure experiment.

Tab. 3: Amount of rain acting on rock tablets during the development of the experiment

Sample and exposure time	Precipitation during exposition (mm)	Accumulated precipitation (mm)
RT 1 # 3 months (oct–dec)	695.25	695.25
RT 2 # 6 months (jan–mar)	174.10	869.35
RT 3 # 9 months (abr–jun)	121.95	991.30
RT 4 # 12 months (jul–sep)	232.95	1224.25

ultimately reach a steady state roughness after the first four months of deployment (after which, changes in roughness are around 1%). The acceleration in the rate of change in roughness is correlated to the amount of rain during the exposure period analyzed. The first trimester was quite humid, achieving 695 mm/month of precipitation, and rock surface roughness increased at the highest rate, whereas the following months' rainfall was below 200 mm/month, coinciding with the low values of rock surface roughness increase (Tab. 3). These data cannot elucidate whether the decrease in the rate of roughness is the result of rain or a gradual approach to an equilibrium steady state controlled by rock grain size. Nevertheless they contribute to understand the first steps in limestone weathering when limestone outcrops are exposed to subaerial conditions (i.e. soil retreat or erosion, rock breakdown, etc.).

Other roughness indices, such as R_a or R_z, present similar trends (Tab. 2). Additionally, rock surface height skewness (*Sk*) and kurtosis (*K*) contributes to a better understanding of the spatial patterns of the first steps of rock weathering. Fig. 2 shows the relation between *Sk* and *K*. If skewness values depart from zero for control samples, for a homogenous grain size rock like our samples, this implies the presence of features such as initial porosity, micro-fractures or joints that introduce noise to the rock surface characterization. Additionally, the kurtosis is larger than 3 indicating that most of the surface heights in each sample are among a small interval of values. Thus, the general characterization of the control samples is a flat surface with some major flaws (Fig. 2). On the other hand, exposed samples show a distinctive pattern; these samples have close to zero skewness and close to 3 kurtosis values (platykurtic), which corresponds to rough surfaces (Fig. 2). This is also clear through SEM images (Fig. 3), where the rock surface roughness increases with exposure time. The main mechanism related with this scenario appears to be the rock cement solution followed by rock grains dissolution and detachment. In that way, the SEM images from 4-month exposed rock tablets show that rock grains are isolated by widening solution (Fig. 3a), and that features such as micro-fractures lose entity as the rock surface is weathered (Figs. 3b, c & d). As follows, it is interesting to address the evolution of parameters such as R_z or R_{max}, which yield values for the exposed tablets close to 2 µm (one order of magnitude larger than non-exposed samples). These roughness in-

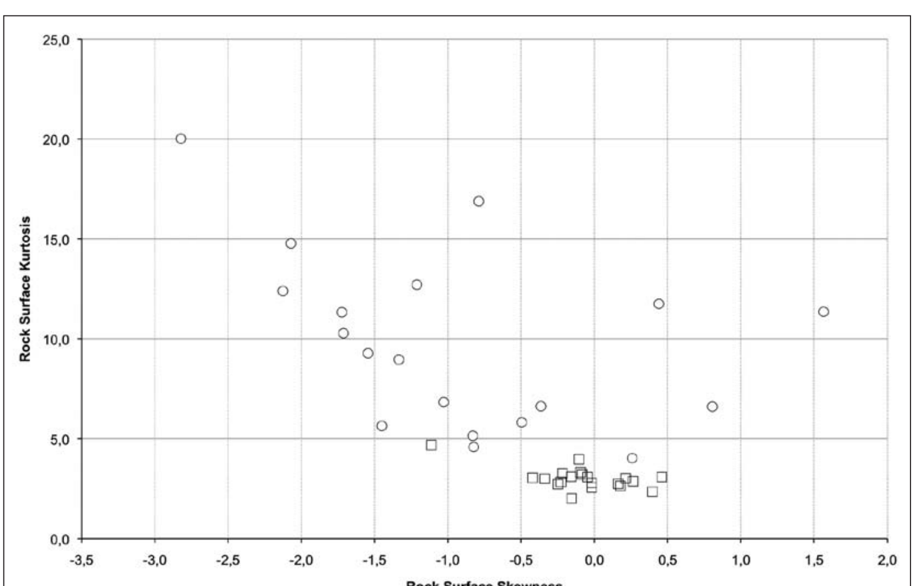

Fig. 2: Rock surface height skewness and kurtosis parameters from non-exposed (circles) and exposed (squares) rock tablets.

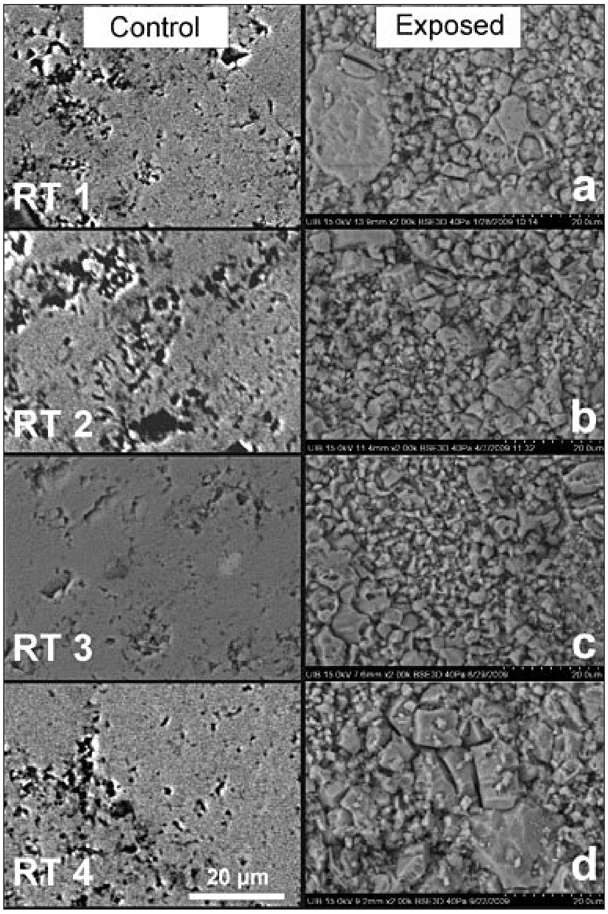

Fig. 3: Rock surface roughness evolution during the exposure period. SEM initial control images before exposition (left column) and exposed samples (a to d) images (right column).

dices, which are equivalent to the absolute difference in height, are similar to the grain size of the rock. Grain size analysis shows a mean of 2.36 µm (1.56 SD) ranging from 0.61 to 13.88 µm. On the other hand, SEM images do not reveal any evidence of biological weathering, only inorganic solution driven processes in the form of crystal controlled solution features, crystal and edge widening and rounding.

Additionally, hypsographic curves (Fig. 4) identify the importance of weathering processes. The graphs indicates the percentage of the rock surface height of the scanned samples above a specific height. As a cumulative representation, a lower percentage represents a higher volume of rock surface below the critical level. Two major interpretations can be made: first, there is general weathering of the surface due to exposure; second, as exposure time increases, there is more impact on the exterior surface of the tablet (i.e. isolated grains) than in the interior of the tablet which can be understood as the bottom of the uppermost sedimentary layer.

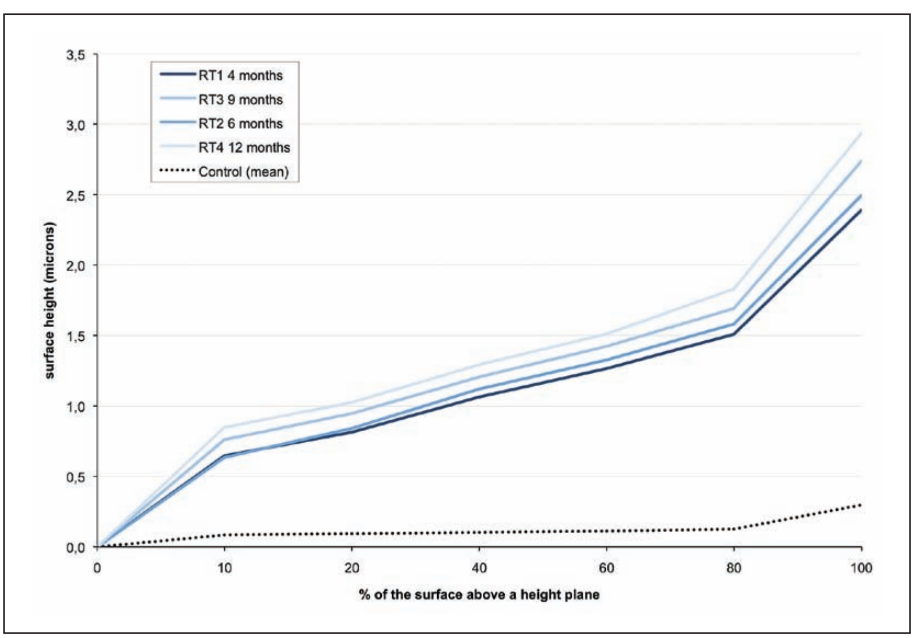

Fig 4: Rock surface hypsographic distribution and evolution.

CONCLUSIONS

AFM and SEM combined studies have been revealed as a key technique for quantifying and characterising the primary steps in limestone weathering and resulting forms. The roughness data values obtained at nanometre and micron scale is visualized through SEM observations. Now we have instrumental observation –far away from black-box deductive frameworks –on the rock surface response to environmental exposure. From exposed data it is clear that bare polished rock surfaces experience a quick increase in rock surface roughness (<4 months under temperate climate in Western Mediterranean) that can result in rock grain detachment due to the preferential solution of grain cement. Future works should constrain the temporal time-scale of first-time exposure as well as determine if a cyclical trend exists every time uppermost grains are fully detached.

ACKNOWLEDGEMENTS

This work was supported by the research fund of MCINN Projects CGL2009-07392 and CGL2010-18616 of the Spanish Government (JJF). LGP is indebted to the "Consejo Superior de InvestigacionesCientíficas" (CSIC) for the funding provided in the JAE-Doc Program. We thank reviewers W.Dreybrodt and M.D. Covington for the constructive and helpful comments to the manuscript. Finally, the authors would like to thank Liana Boop for English smoothing and editing work.

REFERENCES

Crowther, J., 1998: Surface roughness and the evolution of karren forms at Lluc, Serra de Tramuntana, Mallorca.- Zeitschrift für Geomorphologie N.F., 41, 393–407.

DIVMG (Digital Instruments Veeco Metrology Group), 2001. *Command Reference Manual. Software version 5.12 r3*.- Veeco Metrology Group, pp. 617, Santa Barbara.

Dreybrodt, W. & G. Kaufmann, 2007: Physics and chemistry of dissolution on subaerialy exposed soluble rocks by flowing water films.- Acta Carsologica, 36, 3, 357–367.

Evans, I., 1994: General geomorphometry, derivations of altitude and descriptive statistics. In A. Goudie (ed.): Geomorphological techniques, 44–56. London: Routledge, London.

Fiol, L., Fornós, J.J. & A. Ginés, 1996: Effects of biokarstic processes on the development of solutional rillenkarren in limestone rocks.- Earth Surface Processes and Landforms, 21, 447–452.

Gaebel, C., Leadd, J.R., Renshaw, J.C. & J.H. Tellman, 2009: Preliminary indication from atomic force microscopy of the presence of rapidly-formed nanoscale films on aquifer material surfaces.- Journal of Contaminant Hydrology, 108, 46–53.

Ginés, A., Knez, M., Slabe, T. & Dreybrodt, W. (eds.), 2009: *Karst Rock Features – Karren Sculpturing.* ZRC Publishing, pp. 561, Ljubljana.

Gómez-Pujol, L., Fornós, J.J. & J.O.H. Swantesson, 2006: Rock surface millimetre-scale roughness and weathering of supratidal Mallorcan carbonate coasts.- Earth Surface Processes and Landforms, 31, 1792–1801.

Gómez-Pujol, L., Stephenson, W.J. & J.J. Fornós, 2007: Two-hourly surface change on supra-tidal rock (Marengo, Victoria, Australia).- Earth Surface Processes and Landforms, 32, 1–12.

Garbovšek, F., 2009: On concepts and methods for the estimation of dissolutional denudation in karst areas.- Geomorphology, 106, 9–14.

Hillner, P.E., Gratz, A., Manne, S. & P.K. Hansma, 1992: Atomic-scale imaging of calcite growth and dissolution in real time.- Geology, 20, 359–362.

McCarroll, D., 1992: A new instrument and techniques for the measurement of rock surface roughness.- Zeitschrift für Geomorphologie NF, 36, 69.

McCarroll, D. & A. Nesje, 1996: Rock surface roughness as an indicator of rock surface weathering.- Earth Surface Processes and Landforms, 21, 963–977.

Rachlin, A., Henderson, G.S. & M.C. Goh, 1992: An atomic force microscope (AFM) study of the calcite clevage plane: Image averaging in Fourier Space.- American Mineralogist, 77, 904–910.

Ruiz-Agudo, E., Putnis, C.V., Jiménez-López, C. & C. Rodríguez-Navarro, 2007: An atomic force microscopy study of calcite dissolution in saline solutions: the role of magnesium ions.- Geochimica et Cosmochimica Acta, 73, 3201–3217.

Stipp, S.L.S., Eggleston, C.M. & B.S. Nielsen, 1994: Calcite surface structure observed at microtopographic and molecular scales with atomic force microscopy (AFM).- Geochimica et Cosmochimica Acta, 58, 14, 3023–2033.

Swantesson, J.O.H., 1992: A method for the study of the first steps in rock weathering.- Beiträge zur Geölogie, Kieler Geographiscje Schriften, 85, 74–85.

Vies, H.A., 1987a: Blue-green algae and terrestrial limestone weathering on Aldabra Atoll: A SEM and light microscope study.- Earth Surface Processes and Landforms, 12, 319–330.

Viles, H.A., 1987b: A quantitative scanning electron microscopy study of evidence for lichen weathering of limestone, Mendip Hills, Somerset.- Earth Surface Processes and Landforms, 12, 467.

Viles, H.A., 2001: Scale issues in weathering studies.- Geomorphology, 41, 63–72.

Viles, H.A. & C.A Moses, 1998. Experimental production of weathering nanomorphologies on carbonate stones.- Quaterly Journal of Engineering Geology, 31, 347–357.