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## Saltweathering and Porosity - Examples from the Crypt of St.Maria im Kapitol, Cologne

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### Summary

The crypt of St.Maria im Kapitol suffers from extreme salt deterioration. Severe damage to the various rocks and plasters is apparent, which is related to cyclic salt crystallization controlled by changing environmental conditions.

The walls of the crypt are built of three different building stones: a) Sandstone of Kordel, b) a bioclast-limestone and c) Drachenfels trachyte. Each of these rock types shows a different behaviour towards salt deterioration: a) The weathering of the sandstone is leading to granular disintegration, b) on the surface of the bioclast-limestone 1 to 3mm-thick salt crusts are present and c) the trachyte is scaling in 1 to 20 mm-thick stone fragments.

In order to explain the observed differences in physical deterioration, the pore structures and behaviour towards salt deterioration of tile rocks were analyzed using microscopy, mercury-porosimetry, water absorption under vacuum and capillarity and evaporation kinetics.

The observations and investigations of the salt weathering phenomena in situ and of the pore structures have led to the following models for the weathering processes:

a) the Sandstone of Kordel has a relatively high content of intergranular macropores (tailed pores), that interconnect microporous patches mainly lying within the cement, thus evaporation is dominated by water vapour diffusion. This pore structure leads to the crystallization of salts in the micropores and which consequently leads to pushing off single grains to produce granular disintegration.

b) the bioclast-limestone is characterized by a very fine intragranular and well-connected pore system that leads to evaporation and hence crystallization mainly on the surface of the limestone resulting in a mm-thick salt crust.

c) the Drachenfels trachyte has a heterogeneous pore structure, which is built up of small fissures and cracks frequently occurring in or in the vicinity of weathered phenocrysts. Salts crystallize in fissures near the surface, especially near weathered feldspars producing the scaling of fragments up to hand size,

The observed behaviour of each stone type with respect to salt weathering can apparently be explained by the structure of the respective pore system.

### Résumé

La crypte de "St. Maria im Kapitol" est affectée par de fortes détériorations à cause de la présence de sels, qui provoquent de majeurs dégâts aux pierres et aux mortiers.

Les murs de la crypte sont bâtis en trois types de pierres: a) grès de Kordel, b) bioclastites et c) trachytes du Drachenfels. Chacune des trois roches se comporte différemment sous les conditions existantes dans la crypte: a) la détérioration des grès est dominée par la désagrégation sableuse, b) la surface de la bioclastite est découverte d'une croûte de sels d'une épaisseur de 1 à 3 mm et c) dans la trachyte les sels provoquent des éclatements des grandes fragments d'une épaisseur de 1 à 20 mm.

Pour expliquer mieux les différences observées aux trois types de pierres, le milieu poreux a été étudié en utilisant la microscopie, la porosimétrie au mercure, des mesures de la vitesse et de la quantité d'absorption et de la désorption d'eau. Ces investigations en relations avec les observations sur place ont livré les modèles suivants pour expliquer les processus de la détérioration des trois roches. a) les grès de Kordel contiennent une macroporosité assez homogène, qui relie les plages microporeuses. Ces plages microporeuses ne peuvent pas être vidées par transport capillaire mais que par diffusion. A cause de cette structure les sels cristallisent sur-tout dans les plages microporeuses, qui se situent entre les grains de sable; c'est la raison pour la désagrégation sableuse. b) la bioclastite est dominée d'un réseau poreux fin, homogène et très bien lié. C'est pour cela que les eaux sont facilement transportées vers la surface où elles évaporent et les sels cristallisent et forment une croûte. c) le réseau poreux des trachytes est assez hétérogène et dominé par des fissures qui sont souvent situées près des phénocristaux. La cristallisation des sels dans ces fissures provoque les éclatements.

## 1. Introduction

The church St. Maria im Kapitol was constructed between 1015 and 1065 and is situated in the southern part of the centre of Cologne. The history of the church has been documented by FELD (1991). The crypt is situated in the eastern part of the church under the choir, and lies about one third to one half of its height under ground.

During the Second World War, the crypt was partially destroyed. Thus today, only in the eastern part of the crypt remain original building materials consisting mainly of three different rock types: sandstone of Kordel (Lower Triassic), a bioclast-limestone (probably Jurassic) and Drachenfels trachyte (volcanic rock, Tertiary). The walls are partially covered by a sacrificial lime plaster, leaving only portions of the original building stones visible.

The crypt represents a monument with extreme salt damage. In the crypt different salt species are present. The high salt content can be partly explained by the history of the monument: The crypt was used as a salt depot in the 19th century, ground moisture plays a part, alkaline building materials were used, etc. The salt that occurs most frequently within the crypt is a mixture of halite ( $\text{NaCl}$ ) and nitratine ( $\text{NaNO}_3$ ). To a minor degree, thenardite ( $\text{Na}_2\text{SO}_4$ ), mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and trona ( $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ ) also influence the deterioration of the crypt.

The climate of the crypt and the behaviour of the salts were monitored for three years and led to the conclusion that the crystallization of the salts correlates with the climate (LAUE, 1995): During the summer months July, August and September, the crypt is quite moist promoting the dissolution of the dominating salts -the mixture halite/nitratine. By starting the heating system in October small salt crystals of the mixture begin to grow and the intensity of the efflorescences rises until April producing enormous damage. In July the dissolution begins again reinitiating the cycle.

In order to measure the salt content in the interior of the walls, we took drill cores from the three different rocks. On these samples and, where possible, on freshly quarried stones we investigated the pore structures as well as the capillary and evaporation kinetics of the rocks. This paper describes first the observed weathering phenomena of the three rock types in the crypt, then, the capillary and evaporation kinetics and finally, the interpretation of thin sections are given. The connection of all these analyses lead to an explanation of processes that are causing the weathering phenomena of the three rock types. This, we hope, is a further step towards the understanding of the physics of salt deterioration.

## 2. Weathering phenomena in the crypt

Extreme damage to various rocks and plasters is apparent and is related to the salt concentrations of the walls. On the surface of the plaster covered walls, fluffy efflorescences and crusts exist, whereby subflorescences sometimes lead to the bursting of the plaster. Fluffy efflorescences can often be observed in the vicinity of fissures and cracks of the plaster. Crusts of up to a 2 mm. thickness occur probably where a high salt content is present in the wall.

The weathering of the fine-grained sandstone by salts leads to granular disintegration (fig. 1). During the dry winter period sometimes small aggregates of salts form on the surface of the sandstone. In the humid summer period all salt aggregates dissolve. The surface looks damp, but on the surface no drops of a solution can be seen indicating that the hygroscopic solution is sucked up into the sandstone.

On the surface of the bioclast-limestone 1 to 3mm-thick white salt crusts are present (fig.2), sometimes fragments of the limestone are loosened together with the crust and fall off. In the moist summer and the dry winter months no changes of the crust can be macroscopically observed. Probably dissolution and crystallization occur in micro-scale, which can be inferred by analyzing crusts from the limestone under microscope or secondary electron microscop, where several states of dissolution and crystallization periods can be seen.

The Drachenfels trachyte is a volcanic rock characterized by a very fine-grained groundmass with sanidine (potash-feldspar) phenocrysts. In the crypt this rock is, in general, scaling from mm-thickness up to hand-size stone fragments (fig.3). At the surface mm-thin disordered fissures are visible indicating a further break up of trachyte fragments. Often small cracks start at the rim of sanidines. Sometimes small fragments of the groundmass in the vicinity of sanidines are falling off resulting in the protrusion of sanidine crystals on the walls. In dry periods like winter, small patches of salt crust occur on the trachytes surface. In wet periods such as summer, the patches of salts dissolve and form a moist residue on the surface. This hygroscopic solution produces a wet surface on the trachyte, since the solution is not sucked up into the rock by capillary forces.

## 3. Analytical methods

The investigations were executed with at least 3 samples of each rock type taken from dryly drilled cores, whereby one representative sample of each rock type has been chosen to present in this paper. For thin sections the samples were impregnated in the two following way by two differently coloured resins. In the first step red resin was sucked up due to capillary forces filling the free porosity. In the second step the non-filled pores were applied by blue-coloured resin showing the trapped porosity in thin sections.

Porosity accessible to water ( $P_t$ ) and capillarity were determined after RILEM (1980). Porosity after 48 hours ( $P_{48}$ ) was measured by sucking water under atmospheric pressure. The Evaporation curves were executed in a 55% relativ humidity climate after RILEM (1980) with the exception that none of the surfaces of the samples were made vapour tight.

The pore-size distributions were determined with a PoreSizer 9320 of Mikromeritics.



Fig. 1:  
Sandstone of Kordel:  
granular  
disintegration

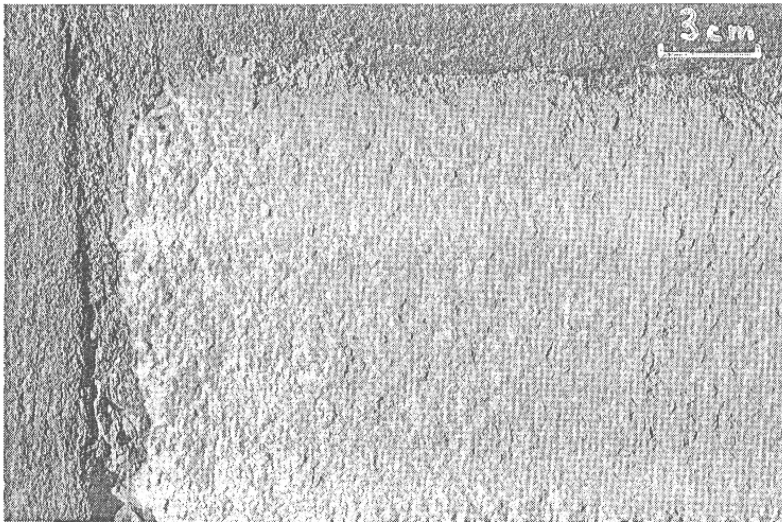


Fig.2:  
Bioclast-limestone:  
a white salt-crust on  
the surface



Fig.3:  
Drachenfels  
Trachyte:  
scaling in  
fragments  
up to  
hand-size

#### 4. Properties of the rocks

##### Capillarity

In fig.4 one typical curve for the capillary rise of water for each rock type is shown. In each graph two curves are drawn: the slopes of the straight lines define the water absorption coefficient A and the water elevation coefficient B respectively, both describing the kinetics of capillarity. The coefficients A and B are calculated by the formulas (HAMMECKER, 1993):

$$A = \frac{dW/S}{\sqrt{t}} \quad B = \frac{h}{\sqrt{t}}$$

The data A and B of each rock sample are listed in table 1.

The water absorption of the three rocks by capillary forces differ considerably. The limestone sucks the water rather quickly (steep curve), and the sandstone shows only a little lower absorption and elevation coefficients, which indicate homogeneous pore structures. In contrast, the trachyte sucks water by capillary forces irregularly, i.e. not perfectly linear with time, suggesting that a heterogeneous pore system is present in the trachyte.

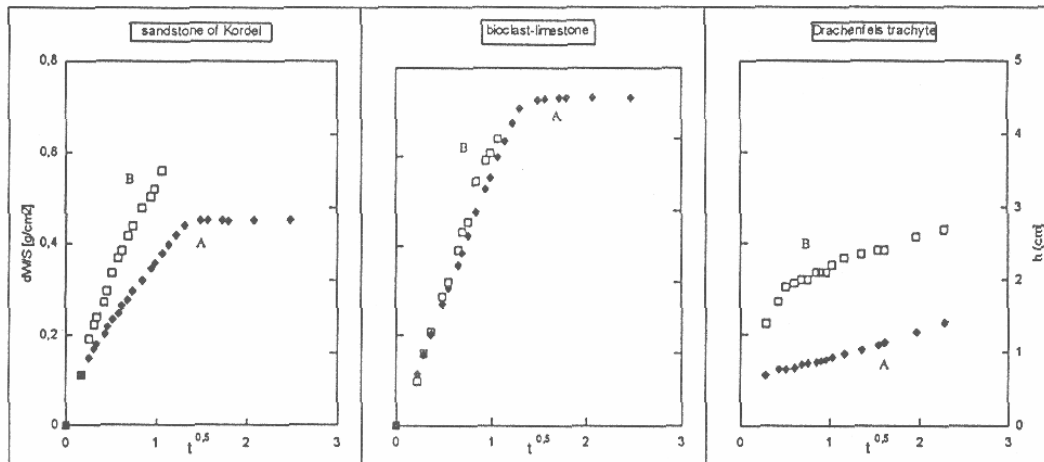


Fig.4: Curves of capillary rise of water, on the left side of each graph the mass of water absorbed by capillary forces per unit area ( $dW/S$  [ $g/cm^2$ ]) and on the right side the height of water ascent ( $h$  [ $cm$ ]) are plotted as a function of the square root of time

##### Evaporation

The evaporation curves (Fig.5) of the building stones are obtained when plotting the density of vapour flow rate evaporating from the sample over time, i.e. weight loss per unit surface of a sample filled with water under vacuum. In general, a curve consists of two parts: in the beginning the moisture content decreases linearly with time until  $Sc$  at time  $T(Sc)$  of the respective samples; this means that the evaporation rate is constant - during this time evaporation takes place near the surface of the sample, whereby the moisture is transported by capillary forces to the surface of the sample. Therefore,  $Sc$ , the critical water content, is defined to be the remaining water content at the moment, when the dominating mechanism of water transport to the surface changes from capillarity to diffusion. After  $T(Sc)$  the rate of evaporation is higher than the supply of water from the interior of the sandstone sample, which

finds expression in the bending form of the evaporation curve. During this second part of the evaporation process the transport mechanism of moisture is diffusion (HAMMECKER & JEANNETTE, 1988), and salt crystallization has to be expected. The data of  $Sc$  and  $T(Sc)$  of the respective samples are listed in table 1.

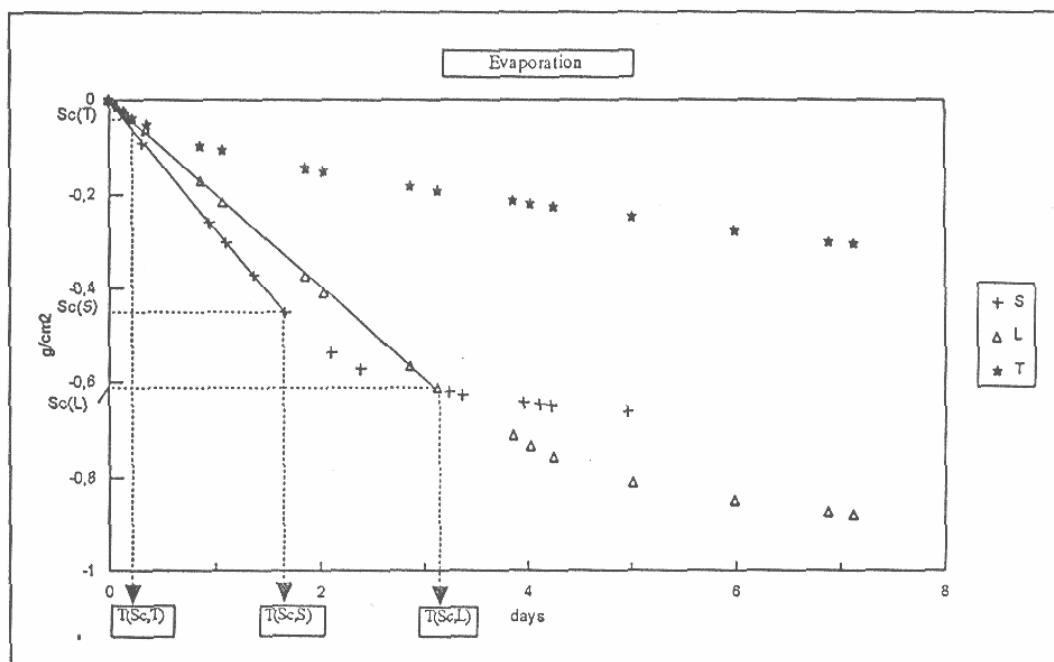


Fig.5: Evaporation curves of the different rocks (S = sandstone, T = Trachyt, L = limestone, explanation see text)

The sandstone of Kordel and the bioclast-limestone lose the same relative amount of water in the initial stage of evaporation (see table 1), but the sandstone reaches its critical water content much faster than the limestone. In both rocks capillary transport processes dominate the movement of a solution to the surface of the samples, where most of the solution evaporates and crystallization takes place. In opposition to that for the trachyte most of the solution evaporates inside of the rock and diffusion is the main moisture transport mechanism. Therefore, the supersaturation of a salt solutions is reached within the rock producing physical stress.

Table 1: Parameters of the properties of the rocks, A = water absorption coefficient, B = water elevation coefficient,  $Sc$  = critical water content,  $T(Sc)$  = duration of evaporation at the surface

	Sandstone of Kordel	Bioclast-limestone	Drachenfels trachyte
A [(g/cm <sup>2</sup> )/t <sup>0.5</sup> ]	0,31	0,56	0,06
B [cm/t <sup>0.5</sup> ]	3,16	3,81	0,18
Sc [%]	37	36	96
T(Sc) [days]	1,7	3,1	0,4

## 5. Porosity

Porosity accessible to water

The porosity accessible to water ( $P_t$ ) is determined by immersion of the sample in water under vacuum conditions. Whereas the porosity after 48 hours ( $P_{48}$ ) expresses the uptake of water after immersion of 48 hours under atmospheric pressure conditions permitting the estimation of the free porosity in the rock (HAMMECKER, 1993). The saturation coefficient  $S$  of the rocks is the volume of water present in the pores after immersion under atmospheric pressure for 48 hours in relation to the total volume of accessible pores. Thus:

$$S = \frac{P_{48}}{P_t}$$

The saturation coefficient  $S$  represents the extent of filled pores by water under atmospheric pressure.

The porosity-data of the different rocks are listed in table 2.

Table 2: Porosity accessible to water ( $P_t$ ), after immersion of 48 hours ( $P_{48}$ ), saturation coefficient ( $S$ ) and Hg-porosity and trapped porosity of each rock type

	Sandstone of Kordel	Bioclast-limestone	Drachenfels trachyte
$P_t$ [Vol.-%]	19,7	19,6	12,5
$P_{48}$ [Vol.-%]	13,3	15,8	8,3
$S$	0,68	0,8	0,67
Hg-porosity [vol.-%]	18,9	15,7	11,1
trapped porosity [vol.-%]	84	60	90

The volume of porosity ( $P_t$ ) in the sandstone and in the limestone exhibit nearly the same amount, whereas in the trachyte the volume of porosity is much lower. Comparing the porosity after 48 hours ( $P_{48}$ ) and the saturation coefficient  $S$ , the pores in the limestone consist of a higher amount of free porosity and therefore can be filled to a higher extent under atmospheric conditions than the pores of the sandstone or the trachyte.

### Hg-Porosimetry

The principles of mercury-porosimetry measurements have been summarized by e.g. PELLERIN (1980). In general, samples around  $1 \text{ cm}^3$  in size are penetrated by mercury under a given pressure, whereby the total volume of penetrating mercury corresponds to the volume of pores with a certain threshold size. After the first intrusion (1) by mercury a desorption process is performed by releasing the pressure. Big pores behind smaller necks (threshold pore sizes) trap parts of the mercury, hence trapped porosity. The trapped porosity determines the amount of penetrated mercury, which can not be desorbed by the desorption process (2).

In a third step (3) the pressure is risen again leading the mercury to reenter the pore system. The three steps are visible in the measurement curves in fig.6, which give an overview of the distribution of the pore threshold size in the various rock types.



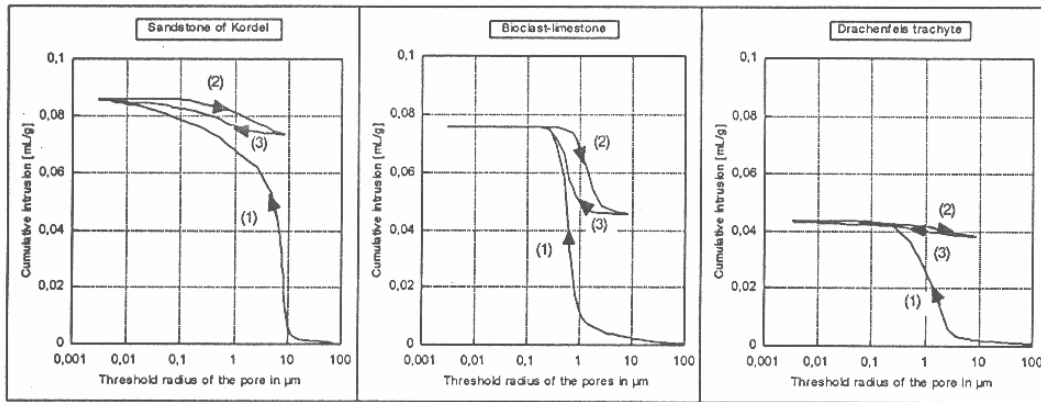


Fig.6: Cumulative intrusion curves of the different rocks, explanation see text

The penetrated mercury in the sandstone corresponds to a porosity of 18,9 vol.-%, the threshold radius lies around 8  $\mu\text{m}$  but only ca. 60% of the total porosity is accessible by pore radii of that size or greater. The trapped porosity is high with 84% of the total Hg-porosity. In contrast to the sandstone, the limestone is characterized by 15,7 vol.-% porosity, whereby the threshold radius of the pores is smaller with ca. 0,7  $\mu\text{m}$ , however it interconnects more than 80% of the total porosity. The trapped porosity in the limestone contains ca. 60% of the total Hg-porosity. The porosity of the trachyte amounts 11,1 vol.-% with an area of threshold radii between ca. 0,2 and 1  $\mu\text{m}$ , ca. 90% of the total porosity lies within this pore size range. The trapped porosity is extremely high with 90%.

## 6. Petrophysics

The evaluation of thin sections, which show free and trapped porosity due to impregnation with differently coloured resins, permits an analysis of pore structures and enables a more precise statement of the size and distribution of pores in relation to the distribution and formation of the minerals involved (HAMMECKER & JEANNETTE, 1988).

The Sandstone of Kordel can be described as a well-sorted lithic arenite consisting of angular to subrounded grains of quartz, feldspar and lithoclasts. The cement consists of secondary quartz, iron oxides and clay minerals. The sandstone is characterized by a homogeneous pore structure with a relatively high content of macropores. Macropores can be observed as intergranular pores (tailed pores), in which trapped porosity dominates in pore-diameters of 100-500  $\mu\text{m}$ . Free porosity exists also in pores ca. < 100  $\mu\text{m}$ , especially in microporous patches at the contact of grains to cement and within the cement itself. The distribution of free porosity in this rock indicates a well connected capillary transport system with macropores interconnecting microporous patches. This is in good correlation to the Hg-porosity, which showed a relatively elevated threshold radius, through that only ca. 60% of the total porosity is filled.

The limestone contains poorly sorted, well-rounded bioclasts in a neosparitic cement, whereby the ratio of bioclasts to cement is around 60 : 40 vol.-%. The porosity in the limestone consists of a very fine homogeneous porestructure defined by inter- and intragranular pores. Free porosity exists throughout the rock mainly as microporosity in scales near or below the resolving power of an ordinary microscope (about 1  $\mu\text{m}$ ). Therefore, the pore structure of the limestone represents a rock with well connected and regarding pore sizes and connectivity very homogeneous capillary transport system.

In contrast to sandstone and limestone, the trachyte contains a heterogeneous pore structure, which is built up of irregularly distributed small fissures and cracks up to several  $\mu\text{m}$  wide.

In the groundmass as well as in the phenocrysts no free porosity can be observed; sometimes in the vicinity of weathered phenocrysts free porosity is present to a small degree. Almost all of the porosity consists of trapped porosity, resulting in a pore system, which is predominantly incapable of transporting solutions by capillary forces.

## 7. Processes of weathering

Considering the observations in situ together with measurements of capillarity and evaporation kinetics, porosity and analyses of the pore structure by microscopy, it is possible to explain the processes of salt weathering of the three rock types in the crypt.

In dry winters a moisture-gradient exists from the interior of the walls to the crypt resulting in transportation of salt solutions from the interior to the surface of the rocks.

The sandstone of Kordel contains a pore system, which is dominated by capillary active pores (threshold ca. 8  $\mu\text{m}$ ) that interconnect microporous patches. When a salt solution evaporates from the surface of this rock, at the critical saturation ( $S_c$ ) only ca. 60% of the porosity is drained remaining ca. 40% of the solution in microporous patches. Below  $S_c$  water transport to the surface takes place by water vapour diffusion resulting in the crystallization of salts in microporous patches. The free porosity observed in thin sections points out the positions, where crystallization of salts takes place: in micropores or in transition zones between micro and macropores predominantly near the surface, which results in pushing off single grains to produce granular disintegration.

The vast majority of all pores of the limestone are accessible by pores of the threshold radius (ca. 0,7  $\mu\text{m}$ ) or greater and the porous system is very homogeneous. The predominant transport mechanism in the limestone is capillarity not only for imbibition but also for drainage, and hence transporting the salt solution right to the surface, where the water evaporates and the salts crystallize to form a crust. In the summer, three months of high relative humidity are not sufficient to dissolve the salt crust. Thus, every year the crust is enriched with salts, which results in the crusts falling off the limestone, when they become too heavy.

In contrast to the above described rocks, the pores of the Drachenfels trachyte are small, consist of fissures and are not well interconnected. Thus, diffusion is the main transport mechanism of water in this kind of rock leaving the salts to crystallize arbitrarily in the porous system and provoking the scaling of fragments. As has been observed microscopically, solutions can penetrate into small fissures or cracks near the surface, especially in the vicinity of phenocrysts and groundmass. When in dry winters the salt solution evaporates, salts crystallize on the surface or in these cracks causing stress, which results in new cracks or leads to the scaling of fragments, partly up to hand size. In moist summers the salts dissolve. Because of the bad capillary connectivity of the pores, the produced salt solution can not be absorbed and is visible in forms of a liquid film on the surface of the trachyte.

## 8. Conclusion

The crypt of St. Maria im Kapitol represents a very good example, where under extreme salt burden different weathering processes can be studied on three different rock types with specific pore structures during changing climate conditions. Transport together with evaporation processes of a salt solution in a pore system define the locations where salt crystallization occur, which is the dominating feature deciding on the type of weathering phenomena. It could be shown that the location of salt crystallization is very much dependent on the pore system, which is described by the amount, the connectivity and the shape of the pores. Thus, by knowing the porous system of a rock it's susceptibility towards salt weathering can be explained.

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