

## Use and conservation of Rhenish tuff

### Effect of moisture on tuffstone weathering

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**Abstract** - Tuffstone elements with a large length/width ratio, as e.g. mullions, often suffer damage in the form of cracks parallel to the surface and spalling of the outer layer. The response of tuff to moisture might be a reason for this behaviour. This research aimed at verifying if a differential dilation between parts with different moisture content (as outer and inner part of partially encased mullion) can lead to damage.

The effect of moisture on the degradation of Ettringen and Weibern tuff has been investigated. A purpose-made weathering test was carried out to simulate the wetting-drying process. Despite no cracks developed during the test, existing cracks widened up and the flexural tensile strength of both materials decreased. The moisture transport properties of the stones were determined as well as their porosity and pore size. Ettringen tuff has a considerable amount of very fine porosity, resulting in slow moisture transport and significant hygroscopic adsorption. Both tuffstones have an extreme hydric dilation. Environmental X-ray diffraction analyses showed that Ettringen tuff undergoes (reversible) mineralogical changes when subjected to RH cycles, whereas this does not occur for Weibern. All results support the hypothesis that moisture gradients in tuff elements may enhance decay in this stone.

### Introduction

Volcanic tuffstone from the Eifel region (Germany), including Römer, Weibern and Ettringen tuffstone, is one of the most important stone types used in Dutch architecture. Römer tuff has been used since Roman times. Weibern tuff has been used in the 15<sup>th</sup> century and from the 19<sup>th</sup> century till half 20<sup>th</sup> century, the latter corresponding to the period of use of Ettringen tuff. Both Ettringen and Weibern tuff are still in use for restoration purposes (Nijland et al. 2003, 2007, 2012, Nijland & Van Hees 2017). Tuffstone is often regarded, not always correctly, as a stone with a limited durability; this may also derive from the fact that the different damage mechanisms affecting tuffstone have not been fully elucidated yet. As a general statement, it is, however, seriously contradicted by presence of building time Römer tuff on several Romanesque churches in the Netherlands.

Besides damage to more conventional weathering mechanisms such as freeze-thaw and salt damage, tuffstone elements with a relatively high length to width ratio, as e.g. mullions and (window) sills, often develop single longitudinal crack in the protruding, exposed part of the element, finally resulting in spalling of the outer layer (Fig. 1, 2). Less commonly, disintegration into fragments of several centimetre to decimetre size may occur. This type of damage is mostly observed

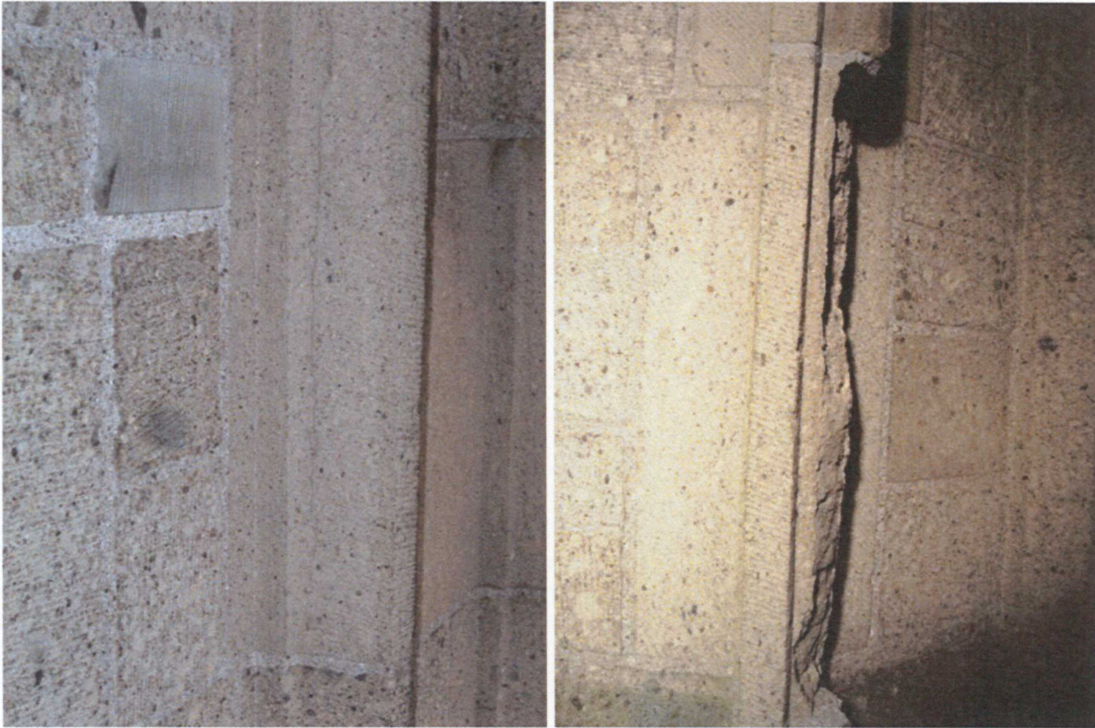
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on Ettringen tuff elements (Fig. 1). It is unclear whether this is due to the nature of the stone itself, or, at least in part, an artefact of the architectural use (Römer tuff is, for example, never used a larger elements in mullions or sills, but nearly always in block) This type of damage also (but much more rarely) occurs on Weibern tuff (Fig, 2), that has been used for similar building elements as Ettringen tuff.

The effect of frost and salt decay on tuffstone has been widely researched in the past (e.g. Schubert et al. 1982, Van Hees et al. 2003, Nijland et al. 2005ab). These, however, do not explain the above described decay patterns. One of the hypotheses is that cracks are due to the hygric-mechanic behaviour of the tuffstone (Nijland & Van Hees 2014). Though some studies exist on the hygric behaviour of Weibern tuff (Franzen & Mirwald 2004) and the relationship between hygric expansion and micropores of various (though not Rhenish) tuffstones (Wedekind et al. 2013). the cause of the above described decay patterns is still unclear. Rhenish tuffstone typically has a high porosity and a bimodal pore size distribution, with both very coarse and very fine pores; these properties result in a high and fast water absorption and a slow drying. When the protruding part gets wet due to rain and dry afterwards, differences in moisture content and consequent hygric dilation may develop between the exposed and the encased part of the stone, possibly leading to stresses at the interface. These stresses may cause damage in the form of longitudinal cracks at the interface and spalling of the outer layer of the stone. This hypothesis has been investigated in this research for both Ettringen and Weibern tuffstone. A purpose-made weathering test was carried out to simulate the wetting-drying process due to rain and sun. An alternative hypothesis that has been put forward, is that initiation of cracks already occurs during tooling by a stone mason, and progressively develops. To evaluate this hypothesis, part of the samples, both mullions and sills, have been chiselled.

Additionally, stone properties relevant to this damage mechanism have been investigated as well.

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*Fig. 1. Typical longitudinal cracking (left) and final damage in mullions of Ettringen tuff at the tower of Eusebius' church in Arnhem, The Netherlands (pictures T.G. Nijland, 2009).*



*Fig. 2. Typical longitudinal cracking (left) and final damage in mullions of Weibern tuff at the nave of St. Peter's church in Leiden, The Netherlands (pictures T.G. Nijland, 2005).*

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### Materials and methods

Fresh quarry Ettringen and Weibern tuff was obtained from a stone mason's company. Both tuffstones come are zeolitized deposits from the Riedener caldera in the Eifel area, Germany (Frenchen 1971, Viereck 1984, Nijland 2015).

The test plan consisted of a weathering test, aiming at simulating in laboratory the wet-dry cycles occurring in the field, and a series of characterization tests, some of them carried out before and after the weathering test. Specimens of different sizes were used for the tests: cubes, prisms, and small scale mullions and window sills. Part of these were simply cut by a saw, and untooled (Fig. 3). Part of the samples have been made in a traditional way by hand a stone mason (Fig. 4), and tooled by a chisel (Fig. 5) for reasons given above.



*Fig. 3. Examples of cut mullion and window sill.*



*Fig. 4. Making of a mullion by hand.*

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*Fig. 5. Example of a tooled mullion.*

The mineralogical and petrographical properties of the tuff stones were investigated by polarized and fluorescent light microscopy (PFM). Specimens were prepared by impregnating the stone under vacuum with a UV-fluorescent resin and then cutting and polishing the samples to obtain thin sections of 25-30  $\mu\text{m}$  thickness. PFM observations were also carried out, together with fluorescent macroscopic observations (FMA, i.e. analysis of polished slabs impregnated with an UV-fluorescent resin), to assess the appearance of damage (cracks, mineralogical changes, etc.) after the weathering test.

The mineralogical composition of the tuffstone was further investigated by X-ray diffraction analysis (XRD) on ground tuffstone samples. Because the type of zeolites present is thought to possibly play a role in the damage process, samples were prepared by removing as much as possible xenoliths and pheno/xenocrysts by hand picking under a binocular, in order to enhance the relative percentage of zeolites. The powers have been ground to a grain size of 20  $\mu\text{m}$ . XRD analyses were carried out by a Bruker D8 Advance X-ray diffractometer in Bragg-Brentano geometry with an anti-scatter screen, without rotation of the sample between 8 and 16° 2 $\theta$  and rotation of the sample between 16 and 66° 2 $\theta$ , a LynxEye detector with an opening angle of 2.945°, primary and secondary soller slits of 2.5 ° and a divergence slit of 0.300 mm. Cu-K $\alpha$  X-rays were generated at 40 kV and 40 mA. Phases were identified by Bruker Eva 2.0 software and the crystallographic databases ICDD PDF2 (2011) and ICSD (2011). The XRD analyses for the identification of the mineralogical composition were carried out at 20 °C / 40 %RH. Additionally, in order to check whether any chemical transformation occurs due to RH changes, XRD diffraction analyses were carried out at different RH's. First, the RH was increased, with steps of 10 %RH, from 40 to 90% and then lowered again, with similar steps, to 10 % RH.

The physical properties of the tuff stones were studied by a combination of methods and techniques. The water absorption of the stone at 20 °C 50 %RH was measured, according to NEN-EN 13755:2008, on cubes 10 x 10 x 10  $\text{cm}^3$  sealed with epoxy resin on the lateral sides. The wetting front in the stones was photographically monitored. After absorption, the specimens were fully saturated

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by immersion in water and then dried at 20 °C / 50% RH through one surface. Their weight was monitored at regular time intervals during drying.

The porosity of the stones was measured according to the RILEM CPC 11.3 (1979) on 4 x 4 x 4 cm<sup>3</sup> cubes. Additionally, porosity and pore size distribution were measured by Mercury Intrusion Porosimeter (MIP) using a Micrometrics Autopore IV9500A. By the use of this instrument pore entrances of diameter size between 0.007 and 366 µm can be measured. Smaller pores were measured by nitrogen adsorption (Micrometrics Tristar 3000 Adsorption Analyzer); adsorption and desorption curves were measured at 77 K (-196 °C).

The thermal and hygric dilation were determined on 4 x 4 x 16 cm<sup>3</sup> specimens. The thermal dilation between 10 °C, 20 °C, 30 °C and 40 °C was measured by means of a dilatometer with a precision of 0.001 mm, after conditioning the specimens at each temperature in a climatic cabinet. Similarly, the hygric dilation was measured after conditioning the specimens at different RH conditions (30%, 50%, 65% and 93%) and in water, at a stable temperature of 20 °C. Additionally, hygric dilation was continuously monitored by means of linear variable differential transformers (LVDT) when cycling the RH between 30 %RH<sup>H</sup> (72 hours) and 93 %RH (24 hours) at a constant temperature of 20 °C during 12 days.

The flexural and compressive strength of the stone was assessed on 4 x 4 x 16 cm<sup>3</sup> specimens, according to NEN-EN 196-1:2005, before and after the weathering test. The load was applied with a speed of 300 N s<sup>-1</sup> and a pre-loading 10 N.

The weathering test aimed at reproducing the wet-dry cycles to which tuffstone mullions and window sills are subjected when positioned in building masonry. A test set-up was developed to this purpose (Fig. 6) consisting of:

- A frame, on which the specimens were placed, positioned on an angle in order to allow flowing away of the water.
- Two pipes with hoses to sprinkle the specimens with water (reproducing rain)
- Four infrared lamp to lighten and warm up the specimens (reproducing the effect of the sun)
- Thermocouples to measure the surface temperature of the specimens. The thermocouples were connected to a computer, so that the intensity of the infrared lamps could be automatically adjusted to keep the temperature constant at 40 °C during the "sunny" period.

The following wet-dry cycle was used: 8 h rain, 64 h drying, alternating a 4 h period of drying at 40 °C and 4 h drying at room temperature. The length of the cycles was chosen based on the water absorption and drying properties of the tuffstone and with the aim of providing an accelerated, but still realistic, reproduction of the situation in the field.

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*Fig. 6. Overview of weathering test (left) and specimens used for the test (right).*

The specimens were sealed with resin on those sides which are normally encased in masonry.

During and at the end of the weathering test, the appearance of new cracks or the widening of existing cracks was visually and photographically monitored. During the last wet-dry cycle, the moisture distribution in the exposed and encased part of mullions and window sills was assessed, before and after the rainy period, by drilling powder samples at different depths and determining their moisture content gravimetrically.

### Characterization

#### *PFM*

The PFM observations show that Ettringen tuff has more stone fragments (basalt, sandstone and schists) and less bims than Weibern tuff (Fig. 7). The bims has been zeolitized and contain inclusions of xeno- and/or phenocrysts (Ti-augite, leucite, quartz, opaque minerals, phlogopite and sanidine). Some holes are filled with calcite.

Weibern tuff has a higher porosity than Ettringen, also because of the presence of a larger amount of bims (Fig. 7). Next to bims, stone fragments (sandstone, schists and siltstone) are present; these are smaller in size and lower in number than observed in Ettringen tuffstone. Xeno- and/or phenocrysts are in this case constituted by Ti-augite, quartz, biotite / phlogopite and tourmaline.

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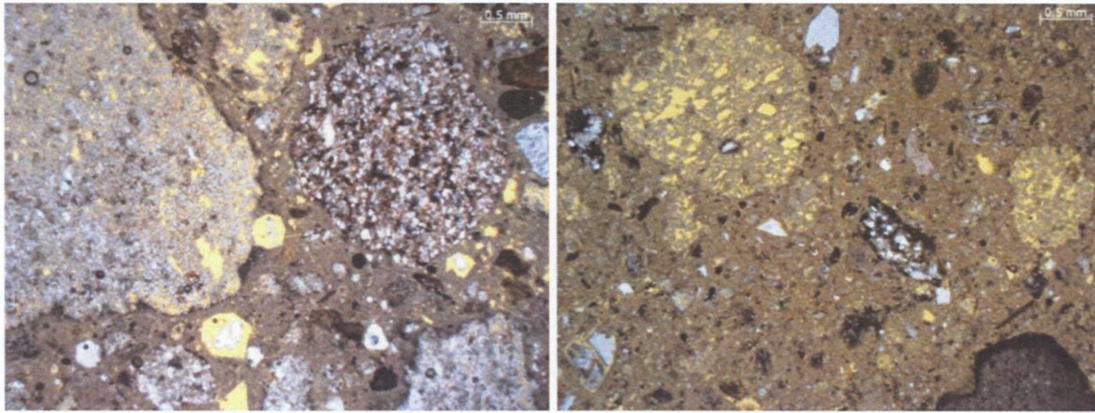


Fig. 7. Microphotographs with an overview of the microstructure of Ettringen (sample TNO 01759; left) & Weibern tuff (Sample TNO 01761; right).

### *XRD analyses*

The XRD diffraction pattern of Ettringen tuffstone (Fig. 8), shows the presence of quartz, albite, sanidine, leucite and clinopyroxene (ferroan diopside, augite, Ca-clinoferrosilite, muscovite) are present, next to philipsite-Ca as the only zeolite. Fitzner (1994) considered philipsite the predominant zeolite in Ettringen tuff. The presence of philipsite as only zeolite in Ettringen has so far only been encountered once in previous studies by our laboratory, other assemblages including analcime (1x), analcime + merlinoite (1x), philipsite + merlinoite (1x), chabazite + philipsite (1x) and analcime + philipsite (2x) (Nijland et al. 2003, 2005, Nijland & Van Hees 2003).

In the Weibern tuffstone, quartz, sanidine, augite, phlogopite and illite are present, next to analcime as the only zeolite (Fig. 9). This is not uncommon for Weibern tuff, in which analcime is the predominant zeolite (Fitzner 1994). It has been encountered as only zeolite five times in previous studies by our laboratory, other assemblages being analcime + chabazite + philipsite (3x) and analcime + gismondine (2x) (Nijland et al. 2003, 2005, Nijland & Van Hees 2003).

The XRD diffraction pattern of Weibern tuff does not change when collected at different RHs. (Fig. 10). Contrarily, the XRD spectrum of Ettringen varies with RH, indicating that chemical transformations occur due to RH cycles; these differences are reversible and seem to be caused by changes in the crystal structure of philipsite-Ca (Fig 11, 12).



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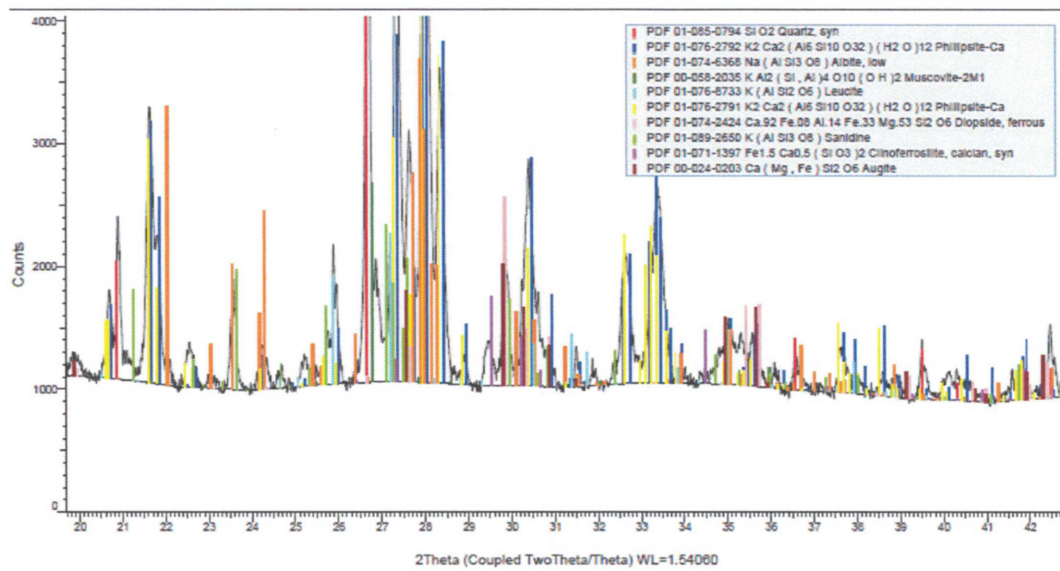


Fig. 8. The XRD pattern of Ettringen tuff, collected at 20 °C and 40 %RH.

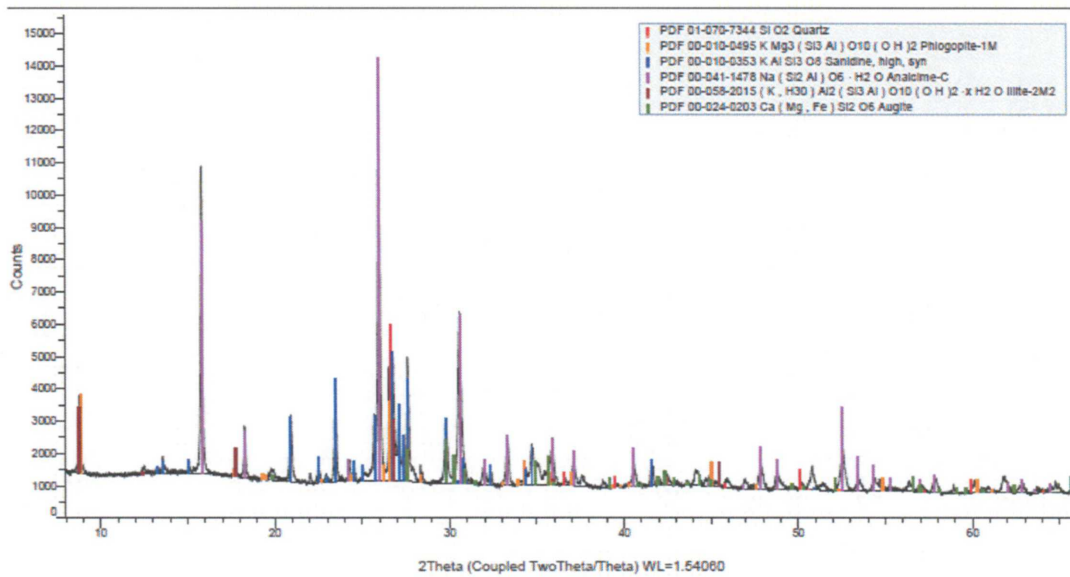


Fig. 9. The XRD pattern of Weibern tuff, collected at 20 °C and 40 %RH.

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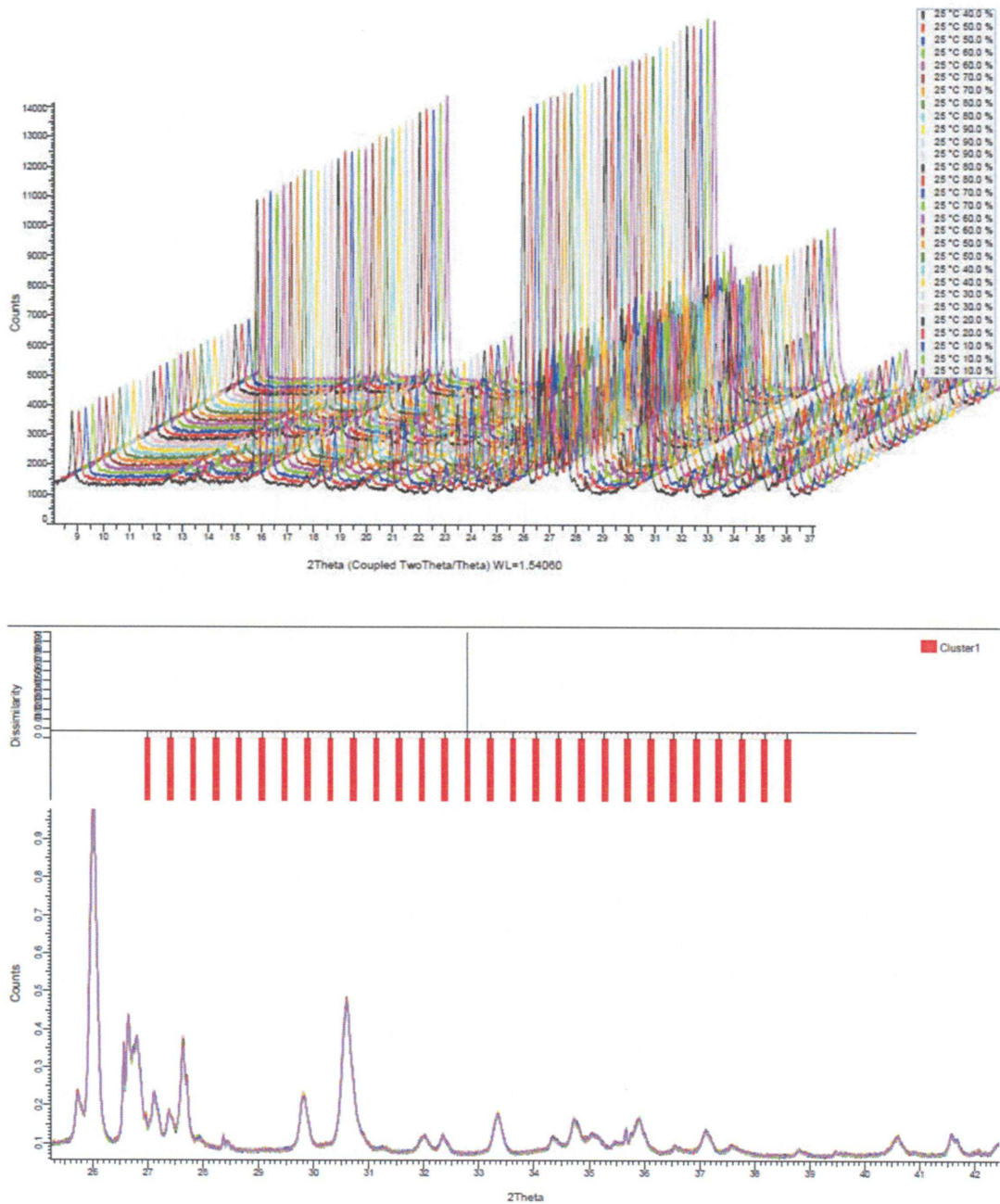


Fig. 10. XRD pattern of Weibern tuff collected at different RH's and 20 °C, above in a so-called cascade plot showing all patterns, below in a statistical cluster analysis of the patterns, showing meaning full differences (in this case none) between the individual patterns over the range 10-90 %RH. Compare figure 11.

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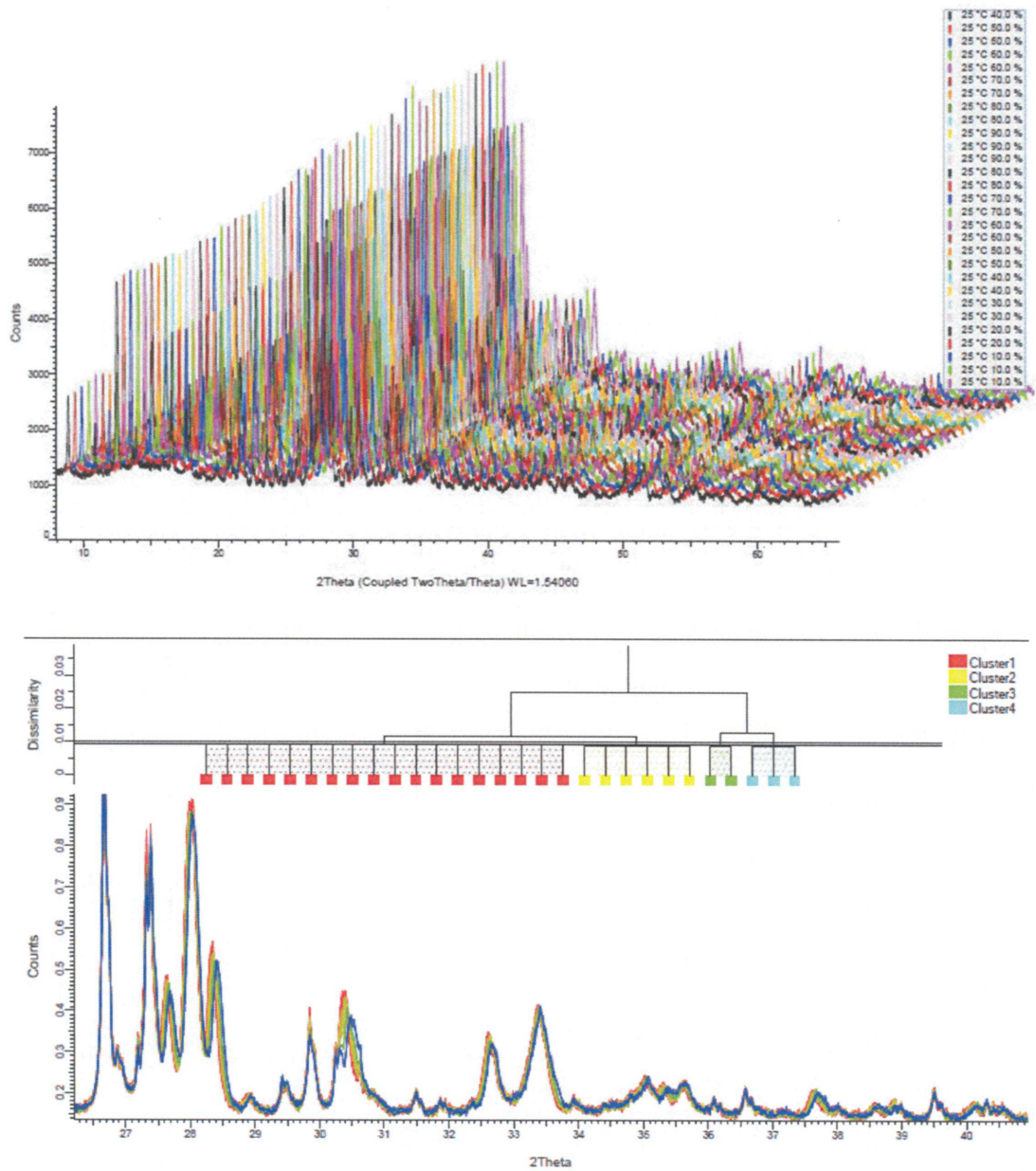


Fig. 11. XRD pattern of Ettringen tuff collected at different RH's and 20 °C, above in a so-called cascade plot showing all patterns, below in a statistical cluster analysis of the patterns, showing meaning full differences between the individual patterns. Clusters 1, 2, 3 and 4 represents RH's of 60-90 %RH, 30-50 %RH, 20 %RH and 10 %RH respectively. Compare figure 12.

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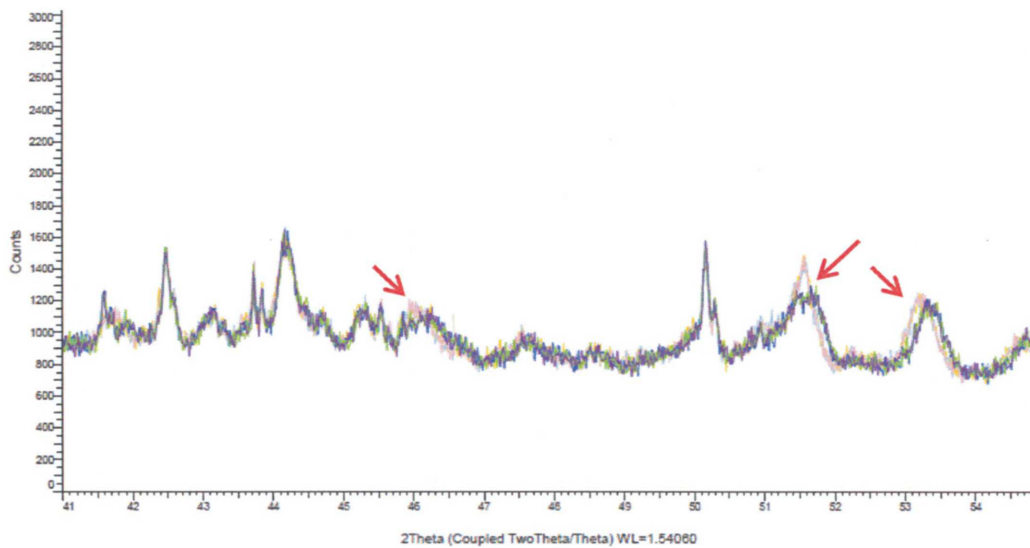


Fig. 12. Part of the diffraction patterns of Ettringen tuff collected at 10 and 90 %RH, respectively, between 41 and 54 °2θ, illustrating the shift in the XRD pattern.

### Porosity and pore size distribution

The total porosity measured by saturation under vacuum according to RILEM CPC 11.3 (1979) is 34.97 vol.% (standard deviation 0.49) and 42.82 vol.% (standard deviation 0.72) for Ettringen and Weibern, respectively. The porosity and pore size distribution of Ettringen and Weibern tuff stones, as measured by MIP, are reported in figure 13. The graph shows that Weibern has a higher open porosity than Ettringen, but their pore size distribution in the range measured by MIP is similar. The open porosity values measured by MIP are (slightly) lower than those obtained by immersion, fact which might be due to the presence of pores larger than 366 μm (largest size measured by MIP) and/or to the lower representativeness of the small samples used for MIP measurements and/or to the presence of some closed porosity.

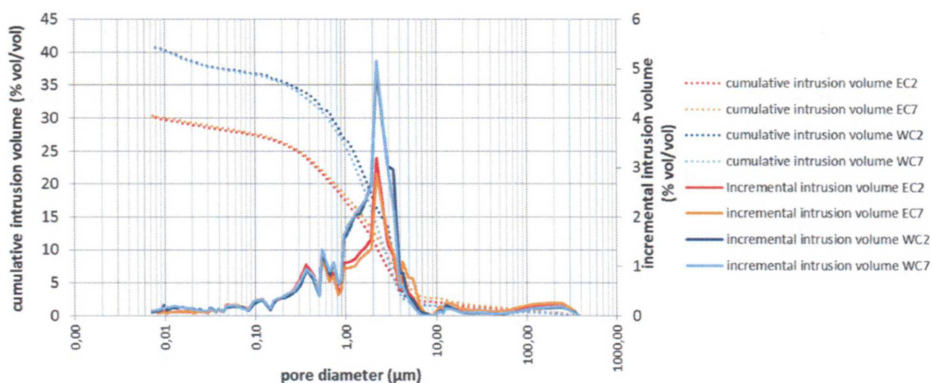


Fig. 13. Open porosity and pore size distribution of Ettringen (EC2 and EC7) and Weibern (WC2 and WC7) tuffstones, as measured by MIP (continuous line: incremental intrusion; dashed line: cumulative intrusion).

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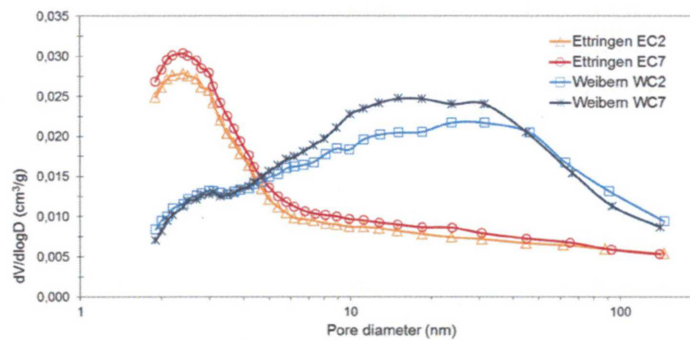


Fig. 14. Pore size distribution of Ettringen and Weibern (W) tuff stones measured (in twofold) by  $N_2$  adsorption.

Pores smaller than  $0.1 \mu\text{m}$  were measured by  $N_2$  adsorption (figure 14). These results show that Ettringen has a larger amount of very small pores (2-4 nm) than Weibern tuff. This can significantly affect the hygric behaviour of the stone.

### Water absorption and drying

Figure 15 shows the water absorption curves of the tuff stones: Weibern has a higher total absorption than Ettringen, fact which corresponds to its higher porosity. The water absorption coefficient (WAC) of Weibern ( $0.316 \text{ kg m}^{-2} \text{ s}^{-0.5}$ ) is higher than that of Ettringen ( $0.064 \text{ kg m}^{-2} \text{ s}^{-0.5}$ ), indicating the faster absorption of the first with respect to the second. The measured WAC for Ettringen is slightly higher than values earlier measured in this stone type ( $0,05 \text{ kg m}^{-2} \text{ s}^{-0.5}$ ; Nijland et al. 2005b); the WAC measured for Weiberner lies in the range reported in literature ( $0.24\text{-}0.38 \text{ kg m}^{-2} \text{ sec}^{-0.5}$ ; Möllenkamp 1996, Franzen & Mirwald 2004, Nijland et al. 2005b). During absorption it was observed that the wetting front proceeds much faster in Weibern than in Ettringen: this difference is probably explained by the pore structure of Ettringen and/or by the presence of very small pores (2-4 nm) in Ettringen tuffstone, which delay the penetration of the wetting front.

The drying of both tuffstones is quite slow: after more than 3 months the specimens are not fully dry yet (Fig. 16). Similarly to the absorption, the drying of the Ettringen stone is slower than that of Weibern.

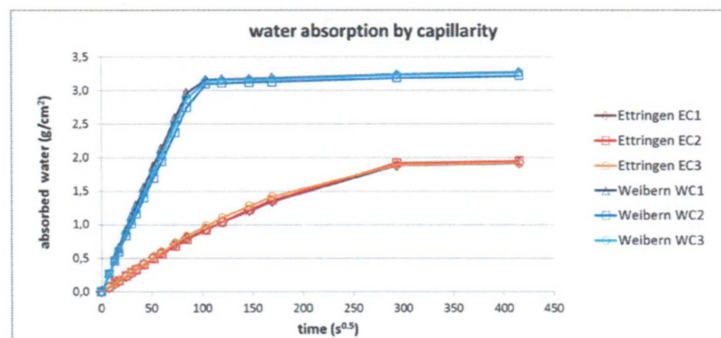


Fig. 15. Water absorption of Ettringen (E) and Weibern (W) tuff stones.

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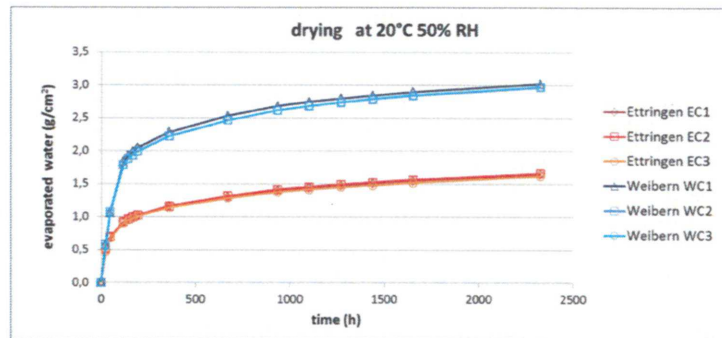


Fig. 16. Drying of Ettringen (E) and Weibern (W) tuff stones.

### Hygric and thermal dilation

The hygric dilation of Ettringen and Weibern, calculated with respect to the specimen size at 20 °C / 30 %RH, is given in figure 17. The hygric dilation of both stones is high, with a maximum of about 1.2  $\mu\text{m mm}^{-1}$ , reached by immersion of the specimens in water. Ettringen tuffstone shows a significant hygric dilation already at low RH. The hygric dilation corresponds to the hygroscopic adsorption of the specimens: Ettringen specimens, due to the presence of very small pores (see above), start to adsorb moisture already at low RH values (Fig. 18).

The reversibility of the dilation was checked by continuously monitoring the dilation during RH cycles. This test shows that the dilation is fully recovered (within the test period). The thermal dilation between 10 and 40 °C at 65 %RH is similar for both tuff stones and equal to 0.15  $\mu\text{m mm}^{-1}$ ; based on these results it can be concluded that the thermal dilation is much less relevant for damage development than the hygric dilation.

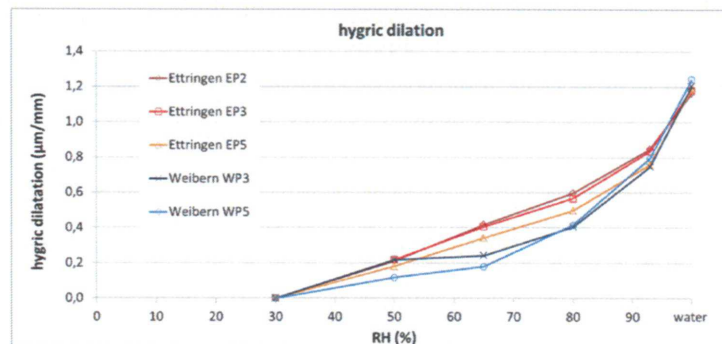


Fig. 17. Hygric dilation of Ettringen (E) and Weibern (W) tuff stones.

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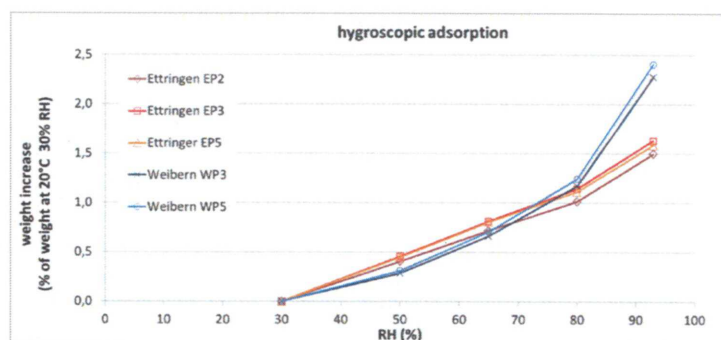


Fig. 18. Hygroscopic moisture adsorption of Ettringen (E) and Weibern (W) tuff stones.

### Mechanical strength

The flexural and compressive strength of the stones before the weathering test are given in table 1. The flexural and compressive strength of Ettringen tuffstone is about double than that of Weibern. The strength values measured for Ettringen tuff show a large standard deviation, indicating that the properties of this tuffstone can significantly vary even within blocks from the same quarry.

Table 1. Flexural and compressive strength of Ettringen and Weibern tuff measured before the weathering test (average of 5 specimens  $\pm$  standard deviation).

		Ettringen	Weibern
Flexural strength	N mm <sup>-2</sup>	8.10 $\pm$ 1.80	4.24 $\pm$ 0.40
Compressive strength	N mm <sup>-2</sup>	29.41 $\pm$ 3.18	13.24 $\pm$ 1.44

### Effect of tooling

In order to evaluate the effect of tooling, i.e. the possibility of crack initiation by a stone mason prior to weathering, samples have been investigated means of thin sections. Neither in the case of Ettringen tuff, nor in the case of Weibern tuff, any cracks have been initiated, confirming previous results on Weibern tuff and Portland stone (Fig. 19; Nijland 2005).

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*Fig. 19. Microphotographs over the bend in a tooled Ettringen (above) and Weibern (below) tuff mullions. Note the absence of any microcracks.*

### Weathering test

The weathering test ran during about 3 months. During and at the end of this period the specimens were visually examined to check the appearance of cracks. According to the supposed damage mechanism, cracks would develop longitudinally, parallel to the exposed surface, in the exposed part of the stone elements. No cracks with these features could be observed with the naked eye. However, the randomly oriented cracks already present before the test seem, based on visual observation, to have widened up. FMA (on all specimens) and PFM (on a selection of 8 samples) observations carried out at the end of the test confirmed the absence of cracks which could be due to the supposed damage mechanism.

During the last wet-dry cycle, the moisture content in mullions and window sills before and after the wet period was gravimetrically determined. The results (Fig. 20) show that the difference in moisture content (MC) between the encased and exposed parts can be high for both mullions and window sills. This implies that



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the difference in hygric dilation between exposed and encased parts can be relevant (see above).

The mechanical strength of the specimens subjected to the weathering test was assessed and compared to that measured before the test (Table 2). A decrease of the flexural strength is observed for both tuffstone types after the weathering test. Differently, the difference in compressive strength before and after the weathering test lies within the range of the standard deviation and is thus not significant.

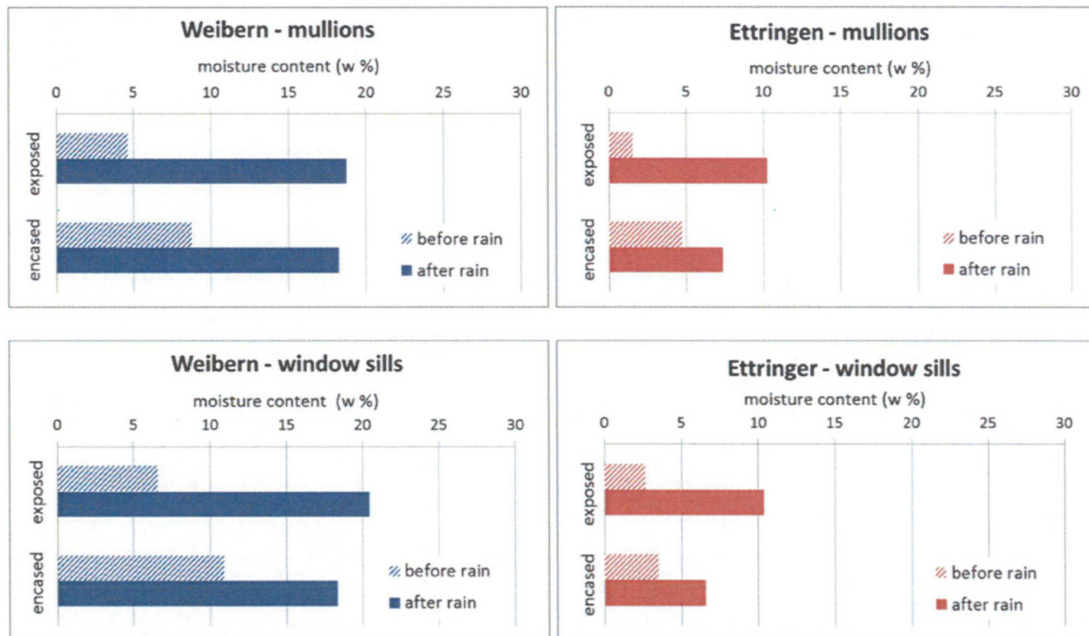


Fig. 20. Moisture content in Weibern and Ettringen mullions and window sills.

Table 2. Flexural and compressive strength of Ettringen and Weibern tuff measured after the weathering test (average of 5 specimens  $\pm$  standard deviation).

		Ettringen	Weibern
Flexural strength	N mm <sup>-2</sup>	6.11 $\pm$ 1.11	3.07 $\pm$ 0.56
Compressive strength	N mm <sup>-2</sup>	27.65 $\pm$ 1.78	14.38 $\pm$ 1.54

## Discussion and conclusions

This research aimed at verifying if a differential dilation between parts of tuffstone elements with different moisture content can lead to damage in the form of longitudinal cracks between the protruding and encased part of tuffstone elements (Fig. 1, 2). To this scope, the effect of moisture on the degradation of Ettringen and Weibern tuff has been thoroughly investigated by means of different methods and techniques. Moreover, a purpose-made weathering test has been carried out to simulate the wetting-drying process. Despite no cracks developed during the test, which could definitely confirm the supposed damage mechanism, the results obtained from the different characterization tests support

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the hypothesis that the hygric behaviour of the stone plays an important role in the decay mechanism of Ettringen and Weibern tuff stones. First of all, because of the presence of both coarse and very fine pores, both these stones show fast water absorption but very slowly drying: this behaviour makes them particularly prone to moisture related damage mechanisms, as biological growth, frost and salt crystallization. Besides, both tuff stones were shown to have a high hygric dilation, which would lead to high stresses at the interface between parts of the stone with different moisture contents, as those which develop during wet-dry cycles. In spite of the fact that the hygric dilation was shown to be reversible (at least in the short term), a decrease in the flexural strength of the stones was measured after the weathering test, suggesting that repeated cycling would lead to weakening of the materials.

Ettringen is to be more sensitive for damage than Weibern due to the presence of very fine (2-4  $\mu\text{m}$ ) pores, which lead to hygroscopic adsorption and hygric dilation even at low RH. The sensitivity of Ettringen to RH is shown also by the mineralogical changes undergone by the stone (most probably by the phillipsite in the zeolites assemblage) during RH cycles. All these factors suggest that Ettringen might be more susceptible to moisture related damage than Weibern. This high susceptibility might be (partially) compensated by its higher mechanical strength.

### Acknowledgements

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