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Original article

Study of internal moisture condensation for the conservation of stone cultural heritage

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ABSTRACT

The natural moisture condensation is considered an important decay factor for stone relics. If protection is only concerned with the conditions under which water forms on the surface, it can cause liquid water to form inside the stone relics over and over again. In this situation, it can lead to considerable damage to the stone relics in fact. In order to investigate the condensed water inside the stone relics, critical conditions have been calculated and a verification experiment has been conducted. The process of the moisture from a gaseous to a liquid state has been studied by several ways, such as the temperature and relative humidity analysis, the resistance and moisture analysis. The situation of both fresh and weathered sandstone samples is considered and analyzed. The results show that the liquid water was produced inside the stone relics before it was formed on the surface when the temperature and humidity gradient distribution from the rock surface to the inner rock is reduced. At last, this paper provides useful guidance to eliminate the harmful effects of the condensed water.

Introduction

The decay of stone cultural heritage exposed to the outdoors is caused by the interaction of numerous factors, natural and anthropic. Particularly, the natural moisture condensation is considered an important decay factor for stone relics [1–3]. The presence of liquid water facilitates chemical reactions of the pollutants, deposited on the surfaces during the dry phase. They may react with the surfaces itself producing crusts, or change the pH of the water and facilitate the dissolution of soluble salts. Moreover, the presence of liquid water aids the growth of biological organisms on the stone.

From the beginning of the twentieth century, many research works have been done about the protection of the stone relics in both China [4–6] and abroad [7–12], which have achieved effective progress. The studies explain the complex interaction between the condensed water and the stone relics [13–18]. The quantitative measurement of the condensed water is available and the corresponding equipments are developed and applied to the physical protection in stone relics such as large-scale grottoes [19, 20]. These works have reduced the atmospheric relative humidity of the grottoes' microclimate and further reduced the condensed water on the stone relics. In the process of treating condensed water, it usually takes the condition of surface produced liquid water as the condition of treatment. According to the long-term monitoring results at Yungang Grottoes [20, 21], it has revealed that the temperature gradient from outside (air and stone surface) to inside (stone interior) is from high to low especially in the summer. In the case of indoor air and rock surface temperature and humidity conditions in Yungang Grottoes not reach the dew point temperature, there will be condensation precipitation on the surface, and we guess that before the surface produces condensate, condensate has formed inside the rock. In addition, when the air temperature and humidity conditions reach the dew point temperature, condensate is generated on the surface, but condensate has been generated internally under this temperature and humidity gradient condition. In our opinion, before the condensed water was formed on the surface of these porous stone materials, the liquid water had been produced inside at a certain depth through the network of pores especially when the indoor air humidity is high during the summer rainy season. If conservation is only concerned with the conditions under which water forms on the surface, it can cause liquid water to form inside the stone relics over and over again. In this situation, it can lead to considerable damage to the stone relics in fact.

In this paper, in order to investigate the condensed water inside the stone relics, critical conditions have been calculated and a

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verification experiment has been conducted. Considering the representation, we used sandstone samples from Yungang Grottoes as the experimental materials. The process of the moisture from a gaseous to a liquid state has been studied by several ways, such as the temperature and relative humidity analysis, the resistance and moisture analysis. At last, the liquid water was produced inside the stone samples before it was formed on the surface when the temperature and humidity gradient distribution from the rock surface to the inner rock is reduced. This paper provides useful guidance to eliminate the harmful effects of the condensed water, enhances the understanding of the formation mechanism of the condensed water inside the stone relics, improves the quality of the conservation of stone cultural heritage.

Research aim

The aim of this study was to investigate the condensed water inside the stone relics. We have conducted an experiment to study the process of the moisture from a gaseous to a liquid state inside the stone relics in order to provide useful guidance to eliminate the harmful effects of the condensed water. It also can be helpful for cultural heritage conservationists to understand the formation mechanism of the condensed water inside the stone relics. The study might improve the quality of the conservation of stone cultural heritage, especially large-scale grottoes.

Methodology

Critical relative humidity (RHc) and dew point temperature (T_d)

In the case of the porous material and within the micropore system, the condensation phenomenon is governed by Kelvin's law, where for each pore radius (r) there is a critical relative humidity, RHc [3]. The effect of surface tension of porous materials can induce condensation inside pores even when temperature is higher than the dew point temperature [3, 12]. Referring to the Kelvin equation, condensation happens inside pores even if the relative humidity is below 100%, and the effect is more relevant in presence of pores with a very small radius. The following equation has been used for the calculation of critical relative humidity values (RH_C) [3]:

$$RH_c = 100 \cdot e^{\frac{-2\sigma_W \cdot V_m}{rRT}} \quad (1)$$

where σ_W is the surface tension of water in air–liquid interaction, 0.072 N/m; V_m is the molar volume of water, 18 cm^3/mol; R is the gas constant, 8.3144621 N m/mol/K; r is the pore radius and T is the temperature of thermodynamic system in equilibrium, K.

The dew point temperature (T_d) is the temperature at which the free water vapor, in humid air at constant barometric pressure, turns from a gaseous to a liquid state and finally accumulates on the cold material surfaces. At 100% relative humidity, the Td is equivalent to air temperature. The Td can be calculated using Eq. (2) based on the August–Roche–Magnus approximation for the saturation vapor pressure of water in air as a function of temperature [3, 8].

$$T_d = \frac{b \cdot lg\left(\frac{P}{P_0}\right)}{a - lg\left(\frac{P}{P_0}\right)} = b \cdot \left[\frac{a}{lg\left(RH \cdot 10^{\frac{a \cdot t}{b+t}}\right)} - 1\right]^{-1} \quad (2)$$

where RH is the relative humidity, 100 > RH >1,%; t is air temperature, 60 > t > 0, °C; a 7.5, b 237.3.

Experimental design

As a world cultural heritage, Yungang Grottoes are a typical representative of the stone relics of the Northern Wei Dynasty, the grottoes are excavated by the mountains, the statues are majestic and magnificent, and the artistic achievements are extremely high. Yungang Grottoes are a large-scale and well-preserved treasure trove of Buddhist art in China and the world, with a history of more than 1500 years. There are 45 main caves in Yungang Grottoes, with more than 51,000 large and small statues. Researchers have made a large number of long-term observations of the microclimate/climate conditions of Yungang Grottoes[20,21]. The sandstone samples used in this paper were taken from the mountain mass on the east side of Yungang Grottoes Scenic Area, and the collected rock samples were homogeneous gray, with no obvious fissures and joint development on the surface. In order to avoid the influence of the superficial regolith layer, fresh rock mass inside more than 20 cm from the surface is selected when mining. One piece of fresh sandstone quarried in Yungang Grottoes was selected with respect to typical of porosity, composition, and diagenesis processes. Then, two studied samples were cut into the same cuboid with size of 200 mm × 120 mm × 120 mm. One was taken as fresh sample and the other one was taken for freezing and thawing test in order to form the weathered sample. The weathered sample has undergone 25 freeze-thaw cycles.

Our experimental treatment process refers to the "Standard for Experimental Methods of Engineering Rock Masses" (GB/T 50,266–2013) standard. Five holes with radius of 7 mm and depth of 60 mm were made in the fresh sample in which to place temperature and humidity sensor. The pretreatment process for stone sample is as follows: 1) drying in oven under 105 °C for 72 h; 2) sealing the sample surface with epoxy resin except the front side and sealing the holes with sealant; 3) standing in a desiccator for 24 h; 4) curing under 60 °C in drying oven. Then the experimental setup can be built as shown in Fig. 1. The environmental control box is used to maintain relatively stable humidity and temperature which one side is open to the front side of the stand sample. One cup of saturated salt solution (75.3% sodium chloride solution) is used for maintaining the humidity that let the water vapor spread to the sandstone sample. One and five (1# ∼ 5#) temperature and humidity sensors (temperature range: −40∼125 °C, RH range: 0∼99%) are separately placed in the environmental control box and the stone sample which the data can be real-time displayed and recorded on computer. The compression refrigeration system (minimum refrigerating temperature: −15 °C) is used for cooling down the stand sample. The insulation resistance tester (maximum measured value: 5.5 GΩ) is used to measure the resistance between the two points in the same position of the two opposing sample sides. The position of five resistance measuring points (1# ∼ 5#) corresponds to the five sensor positions as shown in Fig. 1. Steel nails were nailed to the sample at the position of five resistance measuring points (1# ∼ 5#) before sealing the sample. The microwave moisture system (MOIST350B) [11] measures the moisture of different position of the sample as shown in Fig. 1.

The humidity gradient will form in the sandstone sample after standing for a certain period of time. Then, the compression refrigeration system will work to cool down the sample in order to form the temperature gradient. During the whole process, the data will be recorded and analyzed to find out whether the liquid water is produced.

At last, the weathered stone sample after the same pretreatment is placed in the constant temperature and humidity incubator to form a certain humidity gradient. Then, the same experimental process is carried out to study and validate this problem.

Results and discussions

Fig. 2 shows the scanning electron microscopy (SEM) of the studied fresh and weathered sandstone samples. As the results shows, it is clear that the weathered stone has more fissures than

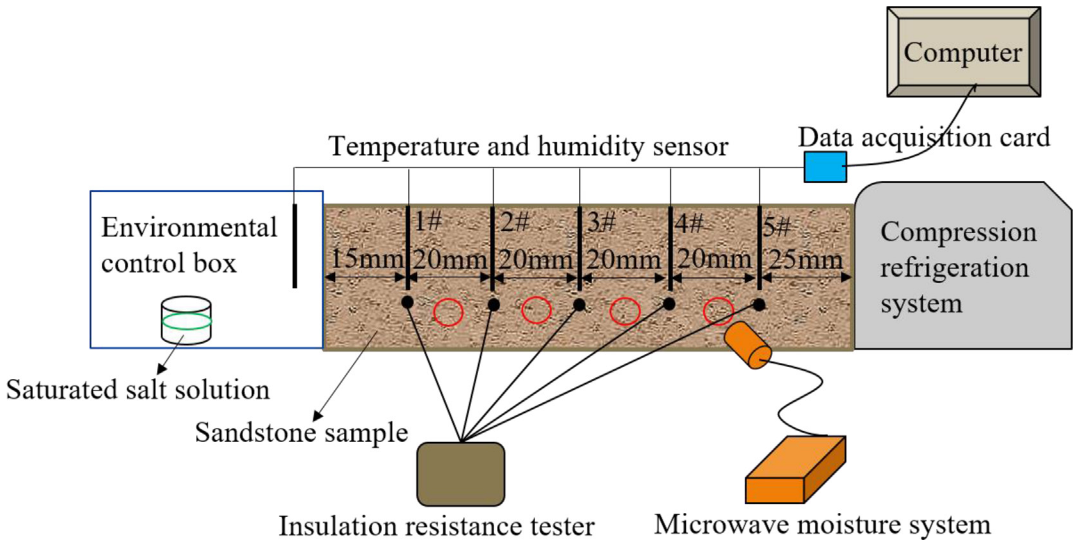


Fig. 1. Experimental setup.

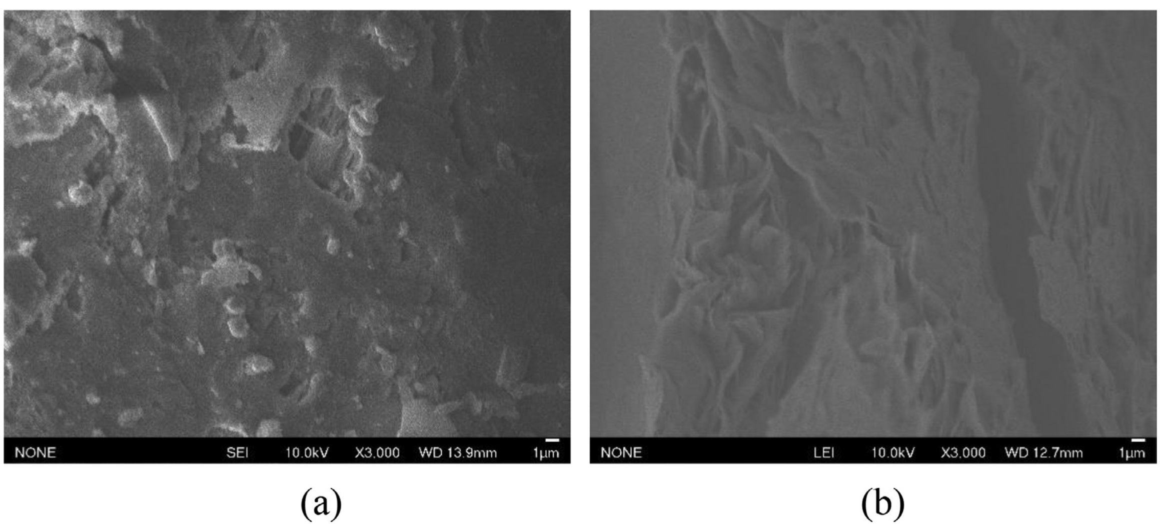


Fig. 2. SEM of studied sandstones. *a*. fresh. *b*.weathered.

the fresh one. These pores and fissures give the stone a porous network ranging between 1 μm and 5 μm, whereas the bigger pores range between among 5 μm and 10 μm. It is also evidenced by the pore size distribution of the fresh and weathered samples.

The pore size distribution was obtained by mercury intrusion porosimetry (MIP) testing. Fig. 3 shows the pore diameter distribution of the studied fresh and weathered sandstone. The pore size distribution of the fresh stone indicates that more than 90% of the pores are in the range of 6.6 $\sim$ 2525.6 nm, which is 18.8 $\sim$ 21,326.4 nm for the weathered one. The red curve shows that the fresh stone has a bimodal pore size distribution, with two main peaks at 150 nm and 600 nm and with a mean pore diameter of about 180.8 nm. The black curve shows that the weathered stone has a monomodal pore size distribution, with one central peak at 700 nm and a mean pore diameter of about 219.1 nm. By comparing the curved lines, it can be seen that the distribution percentage of the weathered stone is lower than the fresh one in the small pore diameter range, which means that the small size holes run through to form the big ones. However, in the big pore diameter range, the distribution percentage of the weathered stone is bigger than the fresh one, which means that many big size holes appear.

Table 1
RH_C of the sample.

Stone sample	Mean pore diameter (nm)	RH_c (%)
Fresh	180.8	98.83
Weathered	219.1	99.03

Considering that condensation occurs inside pores even if the relative humidity is below 100%, RH_C of the sample is calculated by Eq. (3). Table 1 shows the calculated results that the RH_C of fresh one is 98.65% and for the weathered one is 99.03%. It can be seen that the effect of pores on the relative humidity is limited in our study.

Fig. 4 shows the relative humidity of the six sensors over 3 months. The RH in the environmental control box is relatively stable and maintains about 73%. As the water vapor spreads, the RH in the sample rises gradually and shows a certain gradient distribution according to the distance between the 1# $\sim$ 5# sensors and the environmental control box. In order to prevent the influence of high humidity environment on the resistance measurement, the environmental control box was removed and then the compression

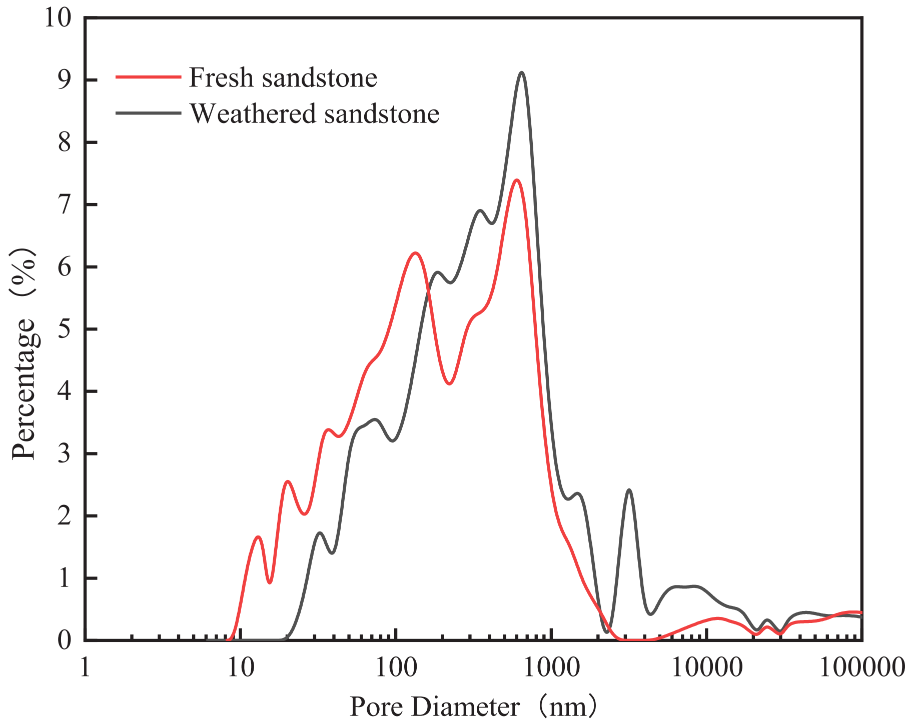


Fig. 3. MIP of the studied sandstones.

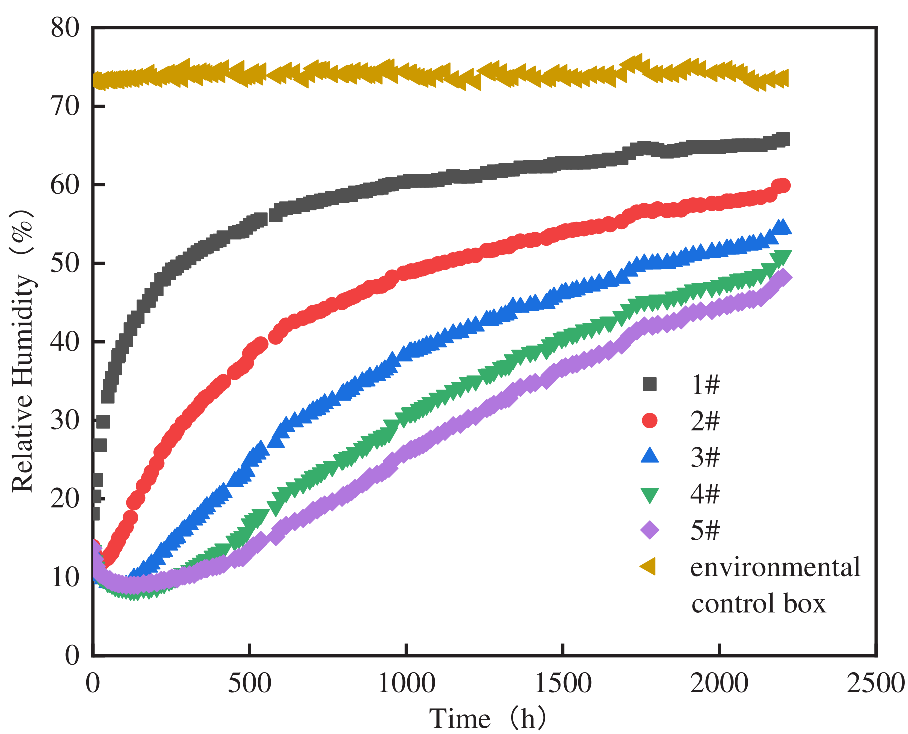


Fig. 4. The recorded RH of six sensors before the cooling treatment.

refrigeration system began to work in a stable experimental environment.

According to the temperature and humidity at the beginning of the cooling, the T_d is calculated as shown in table 2. The corresponding condensation time during the cooling process is listed in Table 2. The resistance drop time in Table 2 is acquired from value distribution in Fig. 7 which shows the measured resistance values according to the position shown in Fig. 1. The resistance, moisture content, temperature and RH were simultaneously measured and recorded during the 3 h of the cooling process.

Fig. 5 shows the relative humidity and temperature of the 1# ∼ 5# sensors. Fig. 6 reflects the distribution characteristics of the moisture content in the sandstone sample in such short time cooling process. The curves separately represents the moisture content of four measurement point which distances from the environmental control box side are 3 cm, 5 cm, 7 cm and 9 cm.

Table 2
T_d, condensation time and resistance drop time for fresh stone sample.

Sensor position	1#	2#	3#	4#	5#	Environment
Temperature (°C)	19.0	19.0	19.0	19.0	19.0	19.0
RH (%)	65.0	59.6	54.7	51.4	48.7	43
T_d (°C)	12.25	10.96	9.68	8.79	8.02	5.11
Condensation time (min)	59	63	62	47	33	/
Resistance drop time (min)	95	65	70	55	55	/

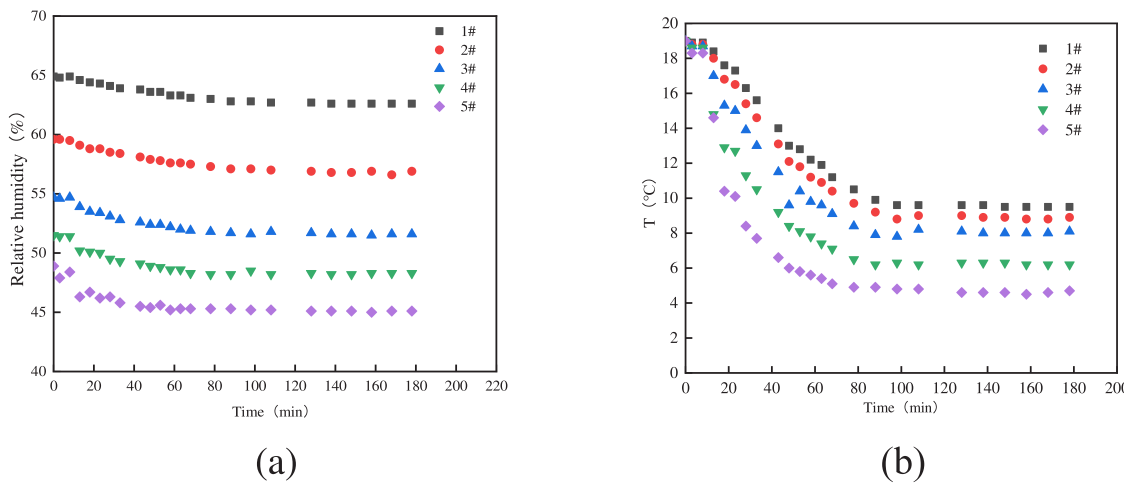


Fig. 5. Relative humidity (a) and temperature (b) of the 1# ∼ 5# sensors.

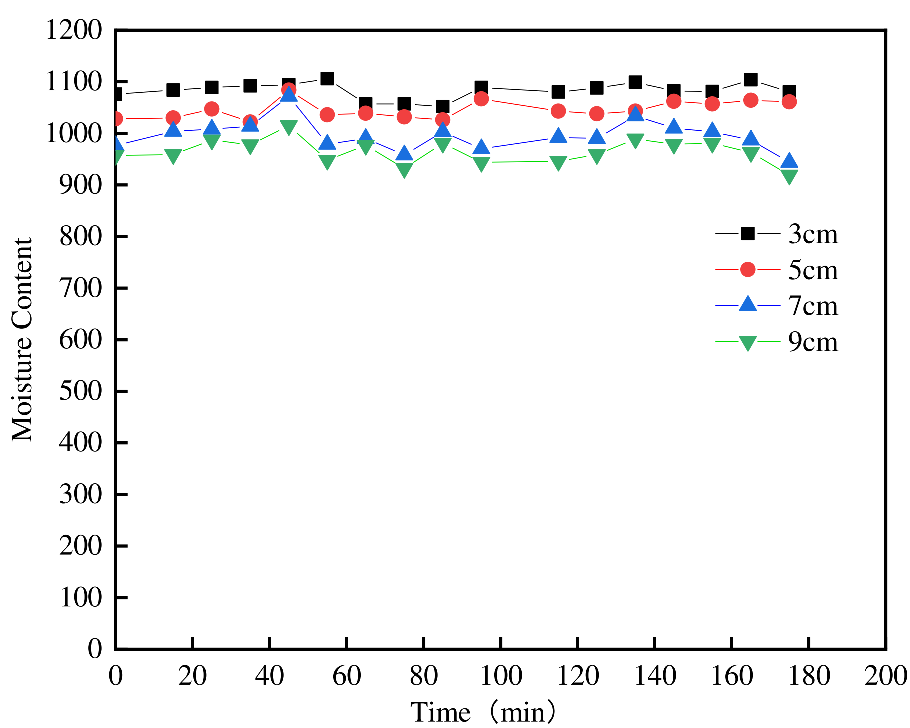


Fig. 6. Moisture content of the sample.

It can be seen that the RH and the temperature are both on a downward trend. The RH values (Fig. 5.a) in the 1# ∼ 5# holes don't rise as the values before cooling process shown in Fig. 4. Since the water vapor spread about 3 months, the moisture got a dynamic equilibrium state in the stone sample. During the 3 h cooling process, the moisture in the holes turned into liquid water, but there was not sufficient supply of water vapor. It is clear in Fig. 6 that the absolute moisture content of the sample changed little with cooling time and the values fluctuated on more than 5%. Therefore, the RH dropped in the cooling treatment.

The condensation time in Table 1 is marked in Fig. 7 with a red line and the resistance drop time seen from the Fig. 7 is also marked with a black line. The resistance values will descend since the moisture in the sandstone turns from a gaseous to a liquid state. It can be seen that the resistance falls down not at the condensation time, namely, the T_d point. According to the experimen-

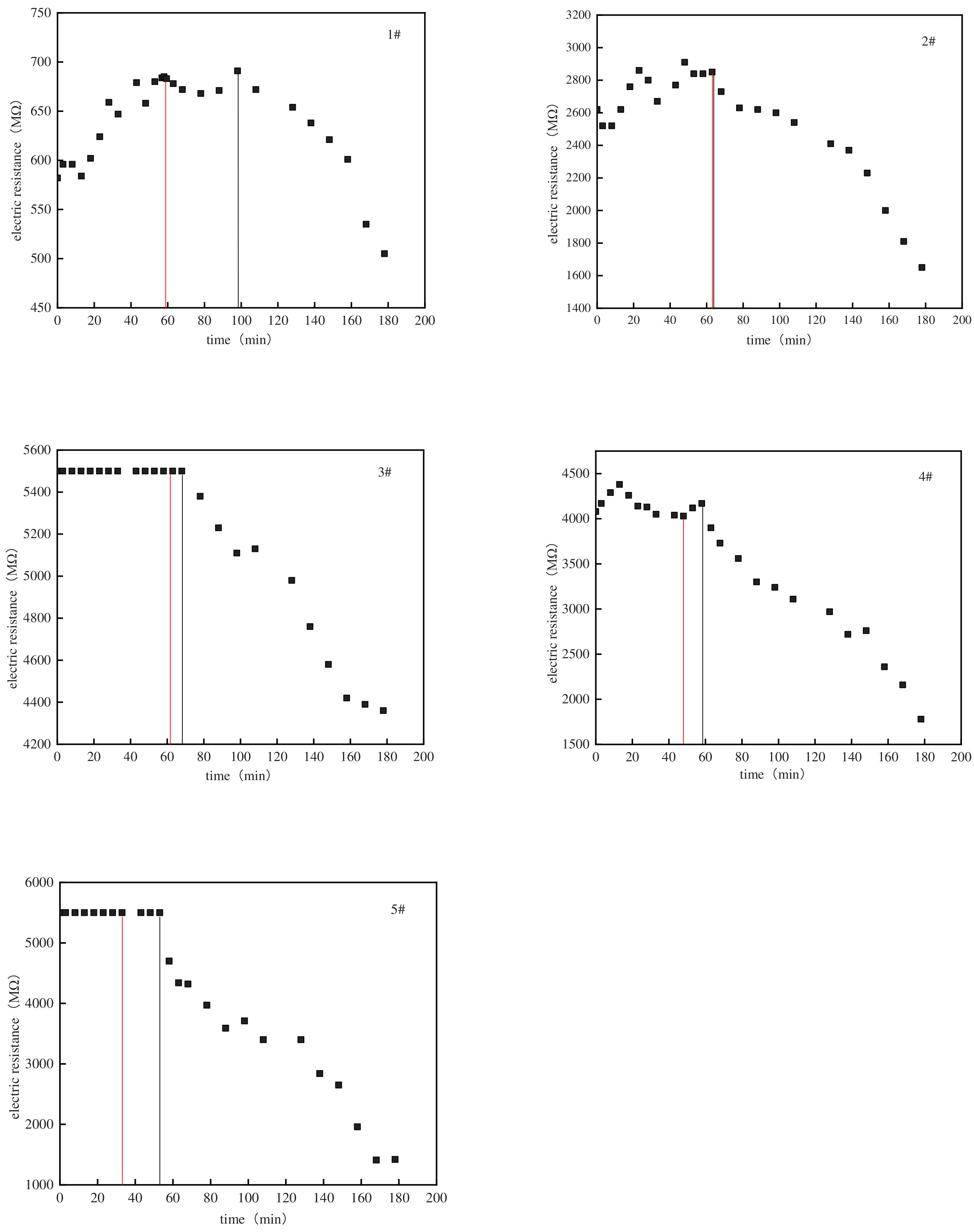
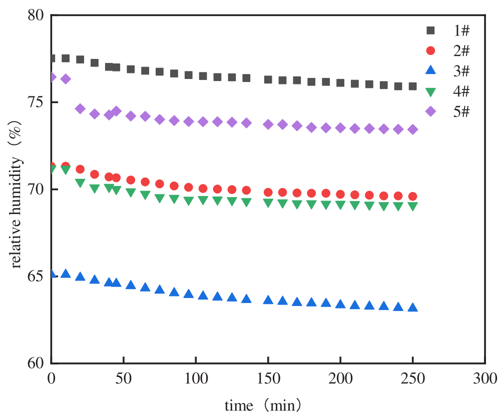


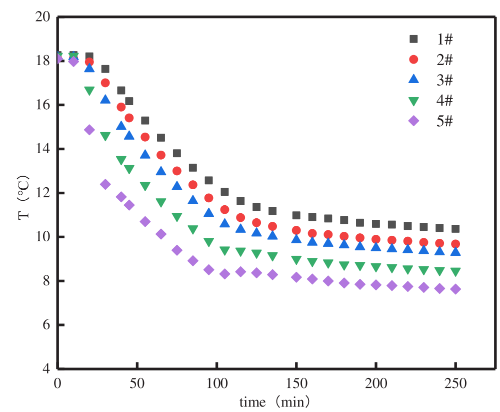
Fig. 7. Resistance value distribution (measuring points: 1# ∼ 5#) of fresh sandstone sample.

Table 3
T_d, condensation time and resistance drop time for weathered stone sample.

Sensor position	1#	2#	3#	4#	5#	Environment
Temperature (°C)	18.2	18.2	18.2	18.2	18.2	18.2
RH (%)	77.52	71.32	65.1	71.2	76.45	50
T_d (°C)	14.27	12.85	11.52	12.92	13.90	7.62
Condensation time (min)	68	77	87	48	23	/
Resistance drop time (min)	210	160	105	75	75	/



(a)



(b)

Fig. 8. Relative humidity and temperature.

tal observations, the electrical resistivity will rise as the sandstone temperature declines. Therefore, resistance values don't drop immediately even when the T_d is reached. The decline of the resistance value illustrates that liquid water was produced after the dew point in the sandstone sample, meanwhile it didn't form liquid on the stone surface. The experiment was simulated based on the monitoring results of the Yungang Grottoes, that is, the temperature was low from the outside to the inside, and the humidity was reduced from the outside to the inside. In our experiments, the temperature and humidity of the surface rocks cannot be monitored, and in this temperature and humidity gradient, the time to reach the dew point temperature inside will be earlier than the surface time, which can be seen from the generation time of the dew point temperature in the experiment. In addition, the first few numbers in Fig. 73# and 5# are almost the same because the insulation resistance tester is out of range, but that doesn't affect the results.

The weathered stone sample after the same pretreatment is placed in the constant temperature and humidity incubator to form a certain humidity gradient. Then, the same experimental process is carried out and the corresponding results are shown in Table 3, Figs. 8 and 9. In addition to an overall downward trend, the humidity gradient in stone sample has a tendency to be high at both ends (1#, 5#) and low in the middle (3#) as shown in Fig. 8(a).

The calculated T_d, the condensation time and the resistance drop time during the cooling process are listed in Table 2.

Fig. 9 shows the measured resistance value of the weathered sandstone sample. It is clear that the values drop after the condensation time. Therefore, the moisture in both the fresh and weathered sandstone samples turned into liquid water when the humidity and temperature meet the condensation condition. In addition, in Fig. 71# and Fig. 91#, 2#, there is too much difference between the time of reaching dew point temperature and the time of resistance decline, which may be related to the rate of temperature reduction, the specific range of the temperature and humidity gradient field, and the amount of water produced under these conditions.

In the case that the temperature and humidity gradient distribution from the rock surface to the inner rock is reduced, that is, the temperature is low from the outside to the inside, and the humidity is also reduced from the outside to the inside, and the inside of the rock will produce condensate before the surface. According to our findings, under the condition of this temperature and humidity gradient field formation, the interior will produce condensate before the surface, that is, the time when the dew point temperature reaches, the interior will be earlier than the surface. This can also be seen from the moment when the dew point temperature is generated. Therefore, the prevention and control of condensation water should focus on not only the surface but also the interior of the stone relics, which is of great significance to the protection of stone cultural heritage.

Conclusion

In this paper, critical conditions have been calculated and a verification experiment has been conducted to investigate the condensed water inside the stone relics. The process of the moisture from a gaseous to a liquid state has been studied by several ways, such as the temperature and relative humidity analysis, the resistance and moisture analysis. The results show that the liquid water was produced inside the stone before it was formed on the surface

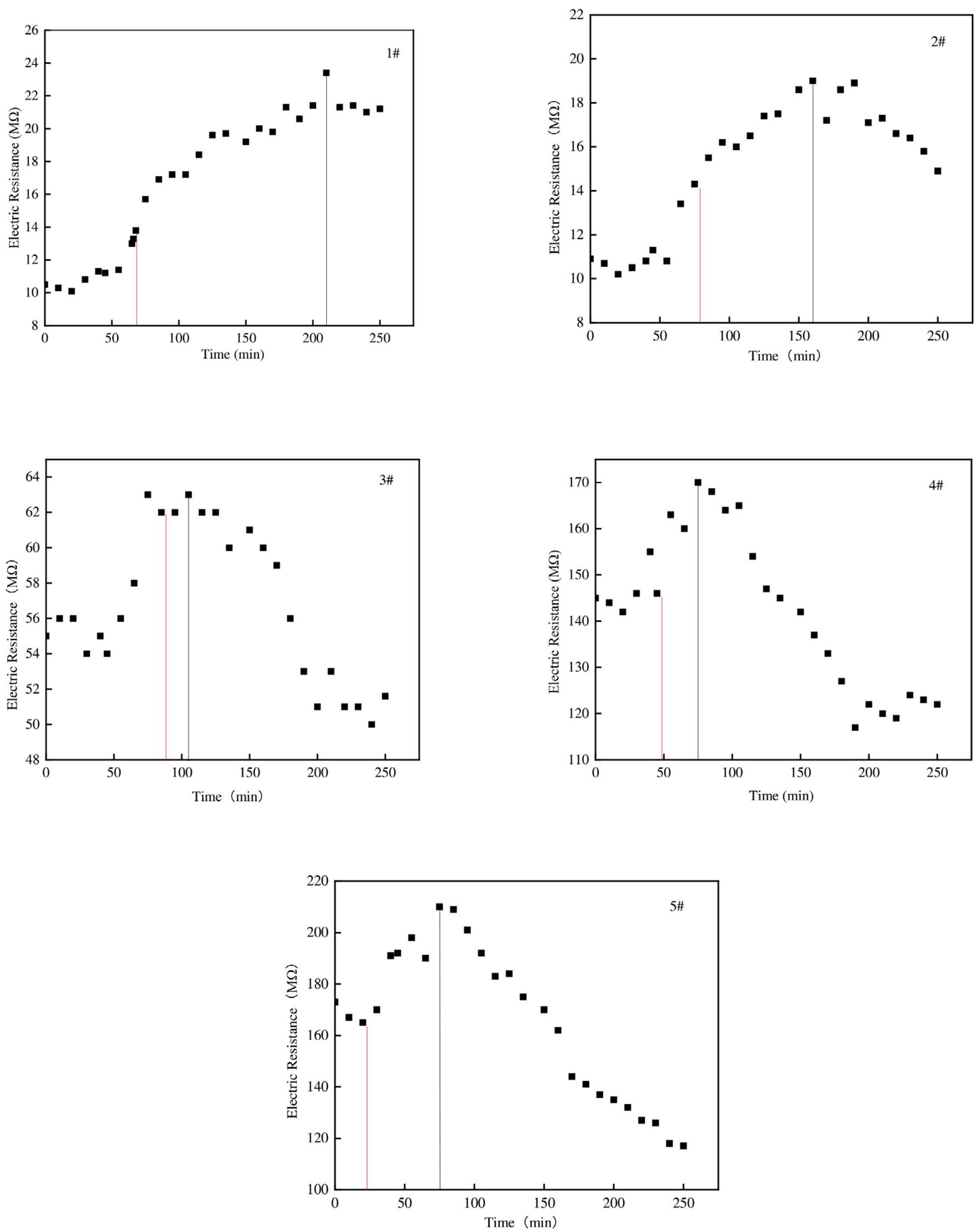


Fig. 9. Resistance value distribution (measuring points: 1# ~ 5#) of weathered stone sample.

when the temperature and humidity gradient distribution from the rock surface to the inner rock is reduced. At last, this paper tells us that the prevention and control of condensation water should focus on not only the surface but also the interior of the stone relics, which is of great significance to the protection of stone cultural heritage.

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