# Salt-induced flaking of wall paintings at the Mogao Grottoes, China

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**Abstract**

The Mogao Grottoes, a World Heritage Site in northwest China, is known for its surviving 492 painted Buddhist cave temples. Commissioned over a thousand year period, from the fourth to the fourteenth centuries, the caves were hewn into a 1.6 km long cliff face and the wall paintings executed on earthen plasters. Situated in a remote and arid desert landscape, these painted caves have endured throughout the centuries but many have also suffered from salt-related deterioration.

Repeat cycles of treatment for flaking on salt-damaged wall paintings have caused worsening of conditions resulting in significant loss of painted plaster. A research project to study this intractable problem and to develop and implement improved treatment methods was undertaken as part of a collaboration between the Getty Conservation Institute (GCI) and the Dunhuang Academy (DA) under China's State Administration for Cultural Heritage (SACH).

This case study looks at the activation mechanisms and deterioration processes of salt-induced flaking and highlights the development and implementation of remedial and preventive measures to prevent further loss from occurring. Topics investigated include the material composition of the paintings and plaster, previous treatments, salt identification and distribution, environmental conditions and the impact of increased humidity. Results show that past treatment of flaking wall painting with polyvinyl alcohol (PVA) and polyvinyl acetate (PVAc) created a film-like barrier that reduced permeability and trapped salts below the painted surface. This led to a build up of salts that when exposed to periods of high humidity caused disruption and powdering of the plaster from cycles of deliquescence and crystallization; the consolidated upper layer, then separated and lifted, in a new form of flaking, referred to as exfoliation.

The study also aimed to improve methods of condition monitoring to better assess when change due to salt activity occurs and to implement findings from the Visitor Carrying Capacity Study for the site. This included identifying caves at risk of salt-related deterioration and closing them to visitation during periods of high humidity.

Keywords: Mogao Grottoes, Dunhuang, wall painting, flaking, salt deterioration, previous treatment

## 1. Introduction

Salt-induced flaking of wall paintings is a condition phenomenon afflicting caves at the Mogao Grottoes, a World Heritage Site in northwest China, known for its 492 surviving painted Buddhist cave temples dating from the fourth to the fourteenth centuries *(Figure 1)*. Situated in a remote and arid desert landscape, these caves have endured throughout the centuries but their wall paintings have been subject to a particular form of loss related to both soluble salt deterioration

*Figure 1: Cave 85, one of the 492 painted Buddhist cave temples at the Mogao Grottoes, was selected as the test cave for this project. Its wall paintings which date from the ninth century suffer from salt-induced flaking.*

and paint flaking, known as exfoliation *(Figure 2)*. Repeat cycles of treatment in past decades have played a role in causing and exacerbating the deterioration phenomena, resulting in significant loss of the cave wall paintings. A joint research project to study this problem was undertaken as part of a collaboration between the Getty Conservation Institute (GCI) and the Dunhuang Academy (DA) under China's State Administration for Cultural Heritage (SACH) with the aim of developing and implementing improved treatment methods as well as measures to prevent this condition from recurring. Improvements in documentation and condition monitoring methods were also undertaken to better assess when changes to the wall paintings are occurring.

*Figure 2: Salt-induced flaking or exfoliation of the wall paintings in Cave 85*

In order to understand the activation mechanisms and deterioration processes of exfoliation, the composition of the paintings and plaster was studied, previous treatment materials and hygroscopic salts were identified, and environmental parameters and visitation history monitored. To provide a complete case study, Cave 85 was selected as a test cave for this project. This ninth century cave has been extensively studied and information was readily available [1].

Treatment of porous, inorganic substrates with synthetic polymers like polyvinyl alcohol (PVA) and polyvinyl acetate (PVAc) can decrease pore size with a consequent reduction of vapor and gas permeability.[2, 3] Upon exposure to high humidity the salts present undergo a phase change, from solid to liquid, and are free to move through the stratigraphy. The less permeable surface, where the synthetic organic materials were applied, can act as a barrier trapping the ions in solution; as the moisture evaporates, the solution becomes saturated, causing the salts to precipitate.[4, 5] Cycles of deliquescence and crystallization then causes gradual decohesion of the lower plaster layer; the upper layers are then separated from the powdering plaster below and are free to lift.

When caves are visited, doors are opened allowing outdoor humid air to intrude into cave interiors. In instances of high humidity, exterior damp air enters rapidly increasing humidity and resulting in damaging salt activity.[6, 7] This aspect of the collaborative project was also part of the implementation of findings from the Visitor Carrying Capacity Study for the Mogao Grottoes that developed visitor management solutions to close caves at risk of salt-related deterioration – including exfoliation – during periods of high humidity.[8] Environmental conditions such as rain and flood events are occurring with increasing frequency causing heightened concern over the long-term preservation of the site and its wall paintings.

## 2. Wall painting technique

Commissioned over a thousand year period, the caves were hewn into a 1.6 km long cliff face of conglomerate rock. Once

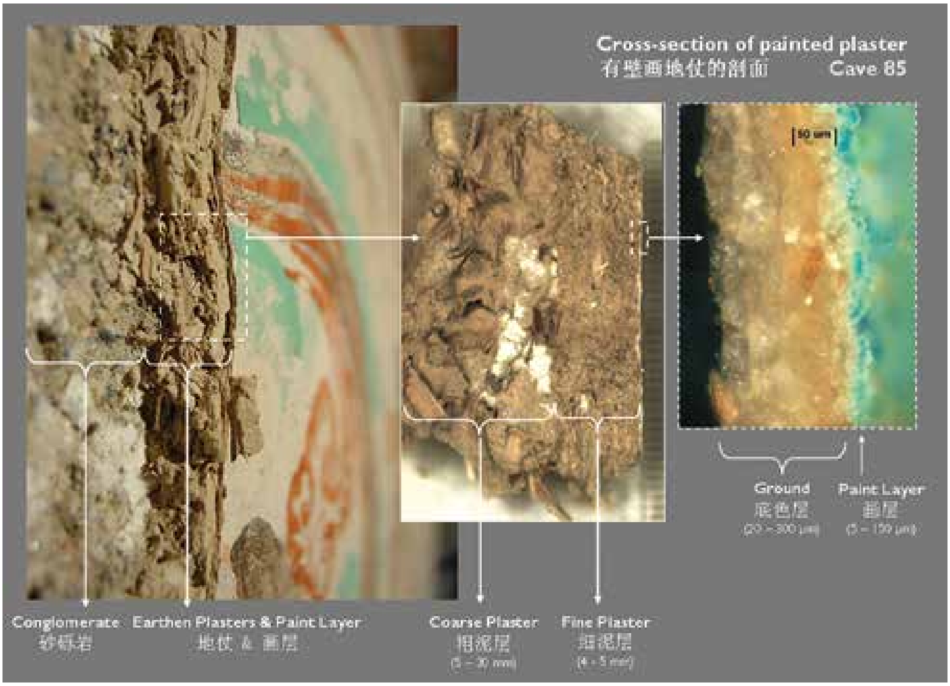


*Figure 3: Stratigraphy of the painted plaster in Cave 85.*

excavated, the roughly carved rock walls and ceilings were plastered and smoothed with a coarse leveling plaster of variable thickness (5-30 mm) and finished with a fine plaster (4-5 mm) *(Figure 3)*. The composition of the plasters were found to be a close match to the riverbed silt from the Daquan River that runs through the site with additional sand and plant fibers mixed in to prevent shrinkage and cracking. The plasters are bound with clay and contain 19% clay-sized fraction including illite, chlorite and the mixed-layer mineral, illite/smectite.[1]

A ground layer, composed of calcium carbonate, talc, and mica and bound with possibly a plant gum or mucilage, was applied as a thin wash to the fine plaster to prepare the surface for painting. Onto the ground, delicate line drawings were executed in red and black ink. The decorative scheme was then filled in with a rich palette of inorganic pigments and organic colorants applied singly or in combination, as thin washes or thick layers, and finished with colored glazes. Because of the variation in paint application, the overall thickness varied considerably (5-150 µm). Analysis found bone glue to be the most extensively used paint medium but samples also showed varying amounts of polysaccharides possibly indicating the presence of plant gums, honey, and mucilage [1].

## 3. Physical history of site and conservation history

Images from the early twentieth century show the site abandoned and the fronts of the cliff eroded leaving the caves open and their wall paintings exposed to the elements. Periodic flooding also occurred in the site's history leading to complete loss of painting up to one meter high in ground level caves and associated moisture and salt-related deterioration in the lower zone of painting.

With the founding of the Dunhuang National Art Research Institute in 1944, doors were installed on caves and beginning in the 1950s full-scale stabilization work on the grottoes commenced. Flood control measures were put in place in the 1960s which prevented occurrences of flooding until June 2011 when a major flood caused substantial damage to the site infrastructure. A subsequent flood occurred in 2012.

Past documentation records show a history of salt-related deterioration exhibited as both surface paint loss and detachment and collapse of painted plaster. In the 1960s, widespread paint flaking was observed in a number of caves and water-soluble synthetic polymers, polyvinyl acetate (PVAc) and polyvinyl alcohol (PVA), were used to treat the paintings, both to relay individual flakes and as a surface consolidant. Today, other adhesives such as gelatin are also being used to treat occurrences of flaking.

In the 1980s, the site was first opened to visitors.

## 4. Condition recording

Paint flaking has been the most prevalent problem at Mogao. During an assessment of 112 caves at the site, seventy-one were found to exhibit this condition making up 63% of the caves assessed.[9] The type of flaking varied considerably from localized to widespread and ranging in severity; sixteen caves exhibited serious and extensive flaking. Salt-related deterioration was found in thirty-four caves making up 30% of caves assessed. Twenty-eight of these are ground level caves with a history of flooding.[9]

In the past, types of deterioration have tended to be looked at individually rather than jointly and as a result salt-related flaking has only recently been identified as a unique phenomenon. A terminology was established to provide a clear and common language for the naming, recording and communicating of information regarding this condition. The terminology also reflects the specific technique of execution of the wall paintings in Cave 85 and focuses on the particular condition phenomena associated with salt-related flaking. Conditions were mapped, macrophotography undertaken and a detailed description of each produced.

### 4.1. Salt deterioration

Conditions related to salt deterioration included plaster disruption which exhibits itself as powdering plaster caused by repeat cycles of salt activity *(Figure 4)*; salt efflorescence seen as salt crystals on the painted surface; and, punctate loss, tiny, rounded losses, less than 1mm in diameter, in the paint, ground and/or fine plaster layer. Salt efflorescence and punctate loss are related conditions: individual salt crystals push through to the surface creating tiny losses in the paint layer. Over time, this gradually leads to complete loss of the paint layer in areas where salt problems are concentrated.

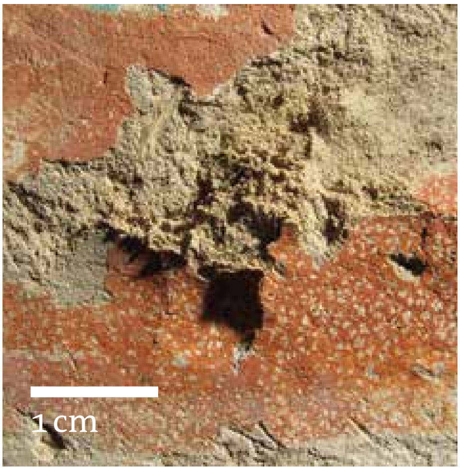


*Figure 4: Powdering and decohesion of the plaster and punctate losses, visible in the red paint layer, are both forms of salt deterioration.*

### 4.2. Paint flaking and exfoliation

Paint flaking occurs when the paint, or paint and ground layer, separate from the layer below and then lifts. This deterioration phenomenon is sometimes referred to as “pure flaking” to distinguish it from “exfoliation” or salt-induced flaking. Exfoliation occurs deeper within the stratigraphy of the painted plaster than pure flaking, typically within the fine plaster layer, and is defined as lifting of the fine plaster and/or ground and paint layers. Exfoliation was found to only occur in caves that have been previously treated for flaking with PVA and PVAc and have active salt deterioration. Exfoliation can be broken down into three stages of development:

1) Decohesion of the plaster due to salt activity causing volume expansion that pushes out the layers above leading to bulging and tenting of the paint, ground and some fine plaster layers. In some cases the protruding area can have associated cracking but otherwise the surface is still closed *(Figure 5a)*.

2) The protruding layers of paint, ground and some fine plaster breaks open along cracks and begins to lift further *(Figure 5b)*.

3) The breakage and opening of protruding areas progresses further to a point where loss of original material occurs *(Figure 5c)*.

Photography alone cannot always accurately describe the extent of lifting, as the way conditions are perceived by the viewer are affected by the angle of incidence of the light on the object. Other documentation techniques were employed to improve characterization of conditions such as Reflectance Transformation

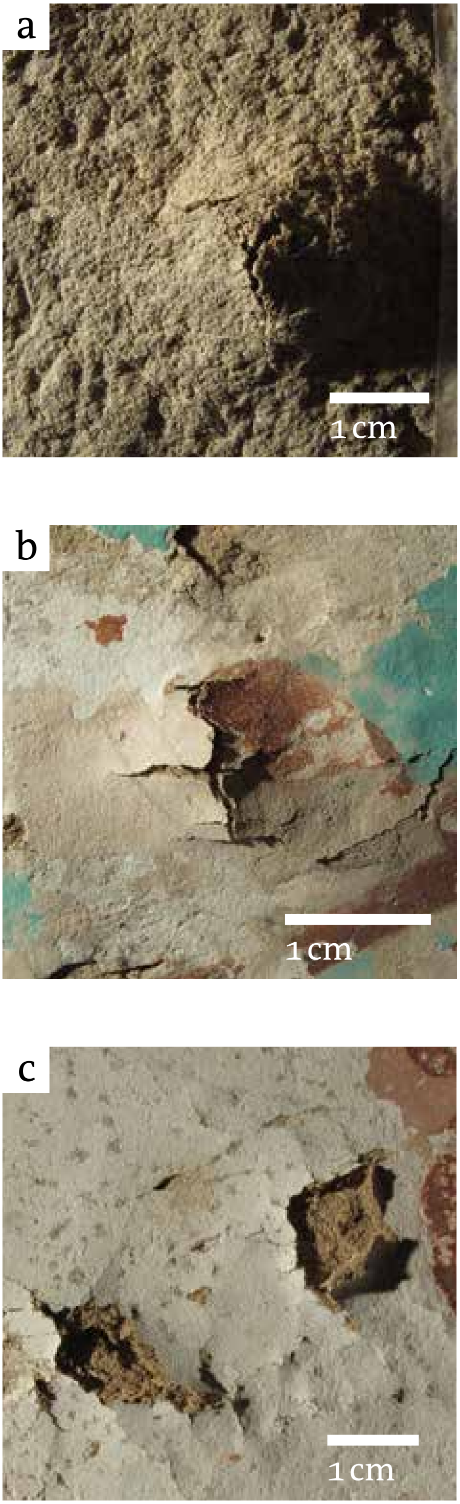


*Figure 5a-c: The three stages of progression of exfoliation.*

Imaging (RTI) which allows you to view an area under different lighting angles.

## 5. Analytical investigation

Sampling of exfoliating layers from Cave 85 was undertaken in areas where deterioration was concentrated. Analytical methods employed included ESEM-EDX on samples mounted in cross-section, FTIR to identify the presence of PVAc, XRD to identify salt species and ion analysis to quantify soluble ions.

### 5.1. Treatment materials

The presence of some treatment materials on the paintings could be seen with UV fluorescence in situ but in general FTIR was undertaken on unmounted samples using an acetone extraction. FTIR can give semi-quantitative information on the concentration of PVAc present on samples, with standardized weight, based on the strength of signal. Out of sixteen samples, twelve indicated the presence of PVAc, two had borderline PVAc present and two showed no positive results for PVAc. Attempts to quantify PVAc content more precisely were unsuccessful.

### 5.2. Soluble salts

The main salts present were identified by X-ray diffraction (XRD) as sodium chloride (NaCl) and sodium sulfate ($Na_2SO_4$).[1] Core sampling at different depths into the clay plaster was undertaken in three caves to provide topographic and stratigraphic distribution.[1] Samples were analyzed with ion chromatography and results indicated that salts were not evenly distributed between caves and within individual caves. Deterioration, however, was found to be correlated with salt content: in Cave 85, areas with the most severe damage had salt content up to 2-3.9% (expressed in weight percent of NaCl per 100gm of plaster) in contrast to less than 1% salt content in areas without visible damage. Stratigraphic soluble ion content for chloride and sodium was highest at the second increment (2-5mm) indicating enrichment of NaCl within the fine plaster and at the interface between the fine and coarse plaster layers.

## 6. Environmental monitoring

Environmental monitoring data was collected from three locations within Cave 85, measuring temperature and relative humidity. The moisture levels in the cave are predominantly influenced through natural ventilation which allows cave air to freely exchange with the outside when cave doors are opened during periods of visitation. Moisture produced by visitors does not significantly contribute to moisture levels in the cave.[10] The impact of the cave door being opened during high exterior humidity is dramatic, causing a sharp and sudden spike in RH *(Figure 6)*. For the most part when a cave is not visited and the cave entrance door remains closed, a fairly stable climate is maintained.[1] However, when high humidity persists for extended periods, the RH inside the cave increases slowly even when the cave door is not opened. The louvered panels and gaps around the door allow humid air to enter.

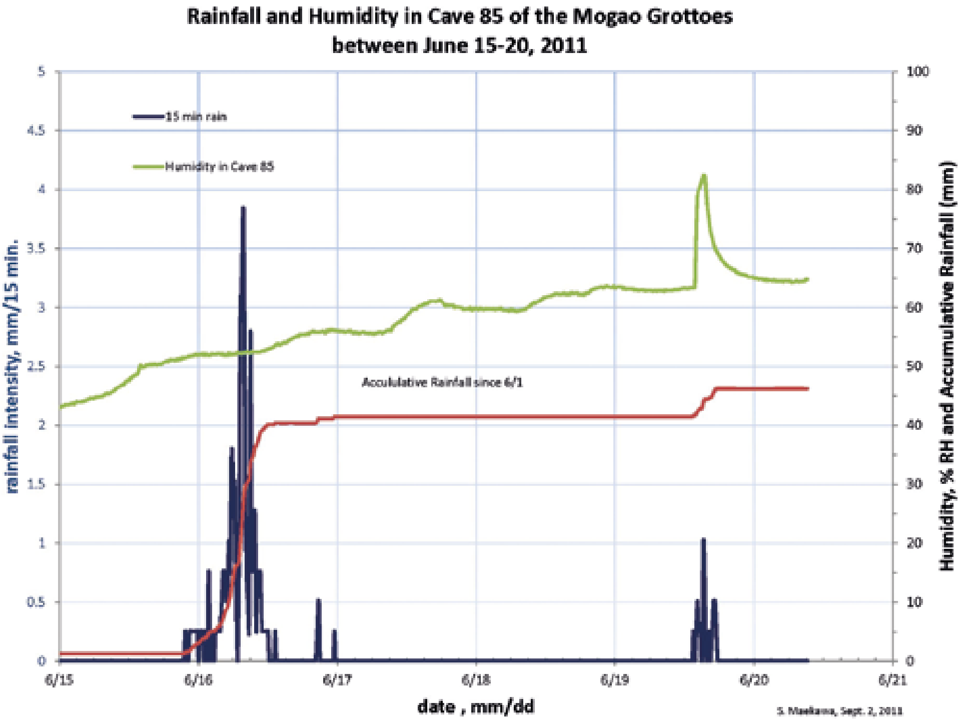


*Figure 6: The humidity in Cave 85 rises even with the cave door closed after a prolonged period of rainfall on 6/16. The sharp peak in humidity that occurs between 6/19 and 6/20 is when the door is opened. In 2011, the RH exceeded 75% several times throughout the summer months.*

## 7. Diagnostic investigation

Caves at the site with a history of treatment with PVA and PVAc were identified and examined. Of these, a few were also found to exhibit salt deterioration and exfoliation. However, there was no corresponding information regarding environmental data and visitation history that could be used to correlate with deterioration. Cave 85 was the only cave where complete information existed.

### 7.1. Linking visitation and environmental data

Visitation information for Cave 85 shows that prior to exfoliation being observed, the cave was opened on a limited basis to visitors. During summer months, several periods of high RH – some of which reached over 80% – were recorded. The repeat fluctuations of RH led to widespread plaster disruption and exfoliation in the parts of the cave where salts are concentrated.

### 7.2. Role of PVA and PVAc

Prior to the use of PVA and PVAc on the paintings, salts would have been able to move through the porous plaster before encountering the less permeable barrier constituted by the paint layer. This caused crystallization within or underneath the ground and paint layers, pushing off the paint layer and leading to punctate loss. Treatment with PVA and PVAc, penetrated into the paint, ground and fine plaster layers, affecting the permeability and porosity of the plaster, creating a less permeable layer. When humidity levels fluctuated, salts present in the plaster, unable to push through to the surface, underwent cycles of crystallization and deliquescence resulting in plaster disruption in the fine plaster. This caused volumetric expansion and the bulging of areas that is characteristic of stage 1 of exfoliation. If conditions persist then stage 2 occurs, where the protrusions burst open; and, then stage 3, when the area continues to open and lift to the point when losses occur.

### 7.3. Humidity chamber

In order to understand the impact of fluctuating humidity on the surface and subsurface layers treated with PVA and PVAc, samples taken from exfoliated areas were placed in an environmental chamber to assess their response to changes in RH (possible moisture uptake and contraction) *(Figure 7)*. The RH in the chamber ranged from approximately 38-86%. A selection of samples were subjected to RH fluctuation and a few showed movement beginning around 60%, indi-

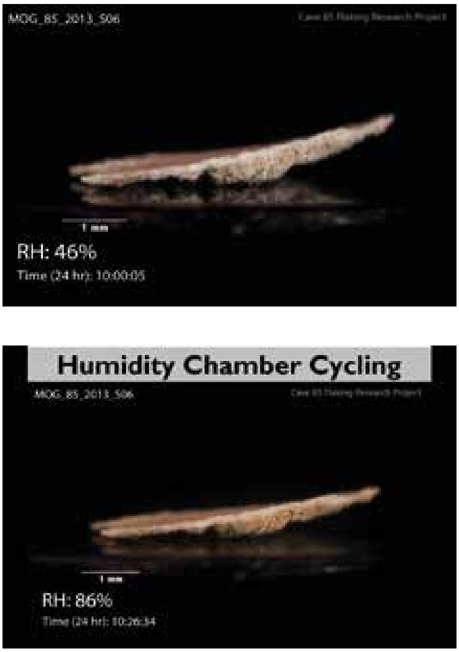


*Figure 7: A sample from Cave 85 placed in an environmental chamber contracted at 46% RH (left) and relaxed at 86% RH (right) in response to changing humidity. Movement in the sample was observed around 60% RH.*

cative of the lifting of layers that occurs with exfoliation. Time lapse images were put together into a short video to record the movement. However, given the complexity of the stratigraphy of the samples including paint, ground, fine plaster plus soluble salts and PVAc – each of which has a different moisture uptake rate – it was not possible to pinpoint the exact reasons for the lifting.[11]

### 7.4. Modeling salt behavior

A salt mixture collected from Cave 85 was tested using Dynamic Vapor Sorption (DVS) between 60% and 75% RH with increments of 0.5% RH.[1] The resulting isotherm showed mass increase starting at 67% RH, as the relative humidity increased, the slope increased exponentially. Salt samples were also examined with ECOS-RUNSALT, a program that uses a thermodynamic model to predict the behavior of salt mixtures under changing climatic conditions 1. However, as salt mixtures can vary depending on the cave and location and conditions of the sampling; and, as different salt species can form depending on the RH, maintaining stable RH and T within a cave was determined to be the best means of preventing future damaging salt activity.

## 8. Remedial treatment

Given that exfoliation is occurring within the fine earthen plaster and in order to avoid adding a film-forming material in the stratigraphy, treatment to relay flakes was undertaken using only water *(Figure 8)*. Water, can act to restore clay binding properties and proved to be an effective means of relaying areas of exfoliation. However, as water can further activate salts, causing damage, and there are water sensitive elements in the painting, treatment trials were undertaken with reduced water content and non-aqueous systems. Water was used mixed with ethanol in varying percentages: 100% water, 50% water: 50% ethanol, 30% water: 70% ethanol, and 100% ethanol. Prewetting with ethanol or ethanol and water (1:1) was also undertaken which helped to soften the layers and acted to consolidate the powdering loose material behind the flakes prior to relaying.

Application methods also aimed to control the quantity of liquid used and to keep the treated area as contained as possible: small brushes were used and the liquid applied through two layers of paper tissue. The flakes were gently pressed back. A Preservation Pencil, an ultrasonic humidifier, was also tested in order to further reduce water content being introduced into the wall paintings but was found to be too slow to be practical.

## 9. Condition monitoring

Photographic condition monitoring of areas treated were established. Context and macro images were taken from different angles and under different lighting conditions both before and after treatment. Microscopy areas were also established to monitor the emergence of salts that may not be visible without magnification. Monitoring aims to be undertaken using the same equipment setup including the photographer, camera and lighting system.

## 10. Conclusions

In all treated areas, exfoliation has not recurred and the decohesive areas of plaster have remained stable. However, in an otherwise arid climate, rain and periods of high humidity are occurring with increasing frequency. Environmental data shows that humidity inside the caves increases even with doors closed. Though

*Figure 8: Relaying of exfoliated areas was undertaken with water and water: ethanol mixes applied with brushes through paper tissue.*

the aluminum door acts to buffer against the outside conditions, recommendations were made to improve the seal by closing gaps around the door and covering louvered panels with non-woven permeable fabric to slow air intrusion. This should be done in conjunction with continued condition and environmental monitoring in order to assess the stabilizing effects this has on the RH of the cave. Finally, visitation to the cave should be managed in a way that does not endanger the wall paintings with a system for closing the caves to visitors during periods of high RH.

## 11. Acknowledgements

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[i] This project builds upon a long lasting partnership between the Getty Conservation Institute and the Dunhuang Academy at the Mogao Grottoes. This includes the conservation of wall paintings in Cave 85 as well as master planning for the site and visitor management [1, 8]. For more information, see: http://www.getty.edu/conservation/our_projects/field_projects/china/app_mogao.html.

[ii] The assessment was undertaken as part of the Visitor Carrying Capacity Study at the Mogao Grottoes by the Getty Conservation Institute and the Dunhuang Academy [8, 9].

[iii] The acetone extraction process consisted of leaving the sample at room temperature for 3 hours then centrifuging it for 10 minutes. 0.2 µl of the solvent extract was then run under FTIR.

[iv] The source of the salts in the Cave 85 wall painting may have originated in the conglomerate substrate, in the original materials of the painted plaster or was brought in with flood events. For complete information on the salt investigation in Cave 85 see Chapter 16, Salt-induced Deterioration of Wong & Agnew 2013 [1].

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