Chemical and physical analysis of sandstone and relationship with weathering damage of Madâin Sâlih monuments

Hayet Khemis Medini and Mgaidi Arbi
Department of Chemistry, Faculty of Science & Arts Al Ula branch, Taibah University, Medina, Kingdom of Saudi Arabia

ABSTRACT
The present work aims to study the effect of weathering - produced sands across the area in the weathering damage of sandstones in Madâin Sâlih (Saudi Arabia). Our approach is to investigate some chemical and physical properties of sand samples from the study area. The weathered point in this arid area is Qsar al Bint or Place of the daughter monument in which five different samples have been collected. The analysis of scanning electron microscope images reveals that sand surfaces have different roughness and some surface areas were broken except for the rock samples. According to energy dispersive spectroscopy analysis, the rock samples reveal the presence of Ca, Mg, Na, K, Al and Fe at the surface. Mineralogy study using X-ray diffraction revealed that sandstones are clay-cemented sandstone. Fourier Transform Infrared spectroscopy analysis confirmed that the inorganic binding agent of silica grains is essentially Kaolonite (Al₂Si₅O₁₀(OH)₄).

ARTICLE HISTORY
Received 13 May 2017
Accepted 15 September 2017

KEYWORDS
Chemical and physical analysis; mineralogical study; sandstone weathering; Madâin Sâlih; sand motion

1. Introduction
Sandstone monuments represent an important cultural heritage worldwide such as Petra, in Jordan and Madâin Sâlih, at Al Ula in Saudi Arabia.

Madâin Sâlih not far from Al Ula (22 km, Figure 1(a)) was known as Al-Hijr or Hegra which is the second most important centre of the Nabataean civilization that occupied this Arabian region two millennia ago (312 BC-106 AD) after their capital Petra, Jordan. The Nabateans carved more than 111 magnificent tombs with many inscriptions and facades which constructed from Lower Paleozoic sandstones (Yellowish sandstones).

Weathering of each façade depends on its orientation. Qasr al Bint “Place of the Daughter or Maiden” which lends its name to the group of adjacent tombs is one of the hewn block in the area, (Figure 1(b)) which is famous for its largest tomb façades with a height of about 16 m (Figure 1(c)). Unfortunately, this place is under constant sand beads attack and presents the more pronounced degradation as it can be seen from Figure 1(d).

It is well known that weathering rate of stone monuments depends on rock type as well as the current environmental conditions [1].

Paradise [2] classified weathering influences in two categories: Intrinsic effects (composition of the rock especially the composition of sandstone matrices, fractures …) and extrinsic effects (human contact, lichen overgrowth, tafoni development, salt crystallization, thermal insulation i.e. solar flux, wind …).

In his previous research, Paradise [3] has concluded that the main factor responsible of disaggregation of sandstone in Petra (Jordan) is the thermal insolation though the sandstone matrices are constituted of iron and silica elements.

Evaluating the surface recessions of sandstones of the ancient city of Pingyao-China semi-arid environment, Zhang et al. [4] pointed out the effect of solar flux on the south and west deterioration sides of the bottom walls. Calcite cement and clayey matrix were confirmed by their petrographic analysis.

Paradise [5] investigated the effect of environmental factors on the tafoni development on the sandstone djinn block Petra, Jordan. The data set collected by this study demonstrates the depending of tafoni development on the direction. For example the southern aspect displayed the longest, widest and deepest tafoni; however, the moderate development was on the northern aspects. As it can be seen from Figure 2(a), the Western faces displayed the tafoni development on Qasr al Bint sandstones. As a first observation, we can say these alveoli are the largest and deepest in the site. The relationship between tafoni assessment and environmental factors will be the aim of our future investigation.

Lichen can be also responsible for biomodification of historic stone surfaces [6]. According to this study, lichen proliferation is dependent on the stone surface temperature and moisture (the difference in the precipitation between the driest and wettest months). For example at Petra, the critical average temperature
threshold is approximately 21°C and the mean annual precipitation is about 298 mm which explains the proliferation of lichen at the stone surface, a phenomenon not observable on a desert climate at Madain Sâlih. Microclimate (wetting-Drying cycles) constitute also an important factor of weathering sandstones [4,7,8].

Figure 1. (a) The Google map of Madain Sâlih location; (b) The Google map of Qasr al Bint location; (c) Full view of Qasr al Bint; (d) Close-up of weathering field.

Figure 2. (a) Broad view of the west facing tafoni development; (b) Full view of Qasr Al Bint looking from the southeast showing the weathering-sand deposition throughout de block.
Studying weathering processes damaging sandstone at Albarracin Cultural Park (Spain) under strongly seasonal climate—mean annual temperature –9°C, Benito et al. [9] concluded that salt and wetting-drying were the main factors leading to rock degradation.

Salt weathering is among the most studied factors. Under Hyper-arid environments, Goudie et al. [10] noted the roles of sodium nitrate and fog in weathering. Fitzner et al. [11] indicated that salt loading of the sandstones is an important weathering factor for damage on pharaonic sandstone monuments in Luxor-Egypt. Salt crystallization and earthquakes were also considered as the most factors that contribute to the damage of Qsar al Bint Petra Jordan [12,13], reported the effect of salt weathering of sandstone on the Angkor monuments, Cambodia. Crystallization of calcite is due to the diffusion of water by capillaries during the raining period. The common conclusion of these studies provides that a sufficient amount of water for dissolution and precipitation and they picked up that the salt weathering mechanisms were complex and still not satisfactorily understood. Some authors suggested that the geochemistry and petrographic composition of sandstones are the meaningful

Figure 3. Localization of sampling, X indicates the position of the sampling.

Figure 4. Histogram of the average grain size distribution of all samples collected from the rock and from the four orientations.
parameters to determine the relationship between weathering rates and chemical composition of the sandstone [14, 15].

According to Benito et al. [9], the clay mineral at the matrix provides the cations exchange and the swelling by external water adsorption. This phenomenon may explain the salt crystallization on the surface. Cardoso and Balaban [16] noted the effect of expansible clay on the deterioration of clay-cemented sandstone.

In the literature, no earlier investigation has approached the processes of sandstones of Madâin Sâlih desegregation or the effect of weathering by wind. Only Vincent and Kattan [17] indicated that the lower Paleozoic sandstones of Al Ula region show a remarkable yardangs with downwind transition and a dune field. Indeed, during summer, northwesterly winds blow frequently and very strong causing dust storms which probably explains the different amount of sand deposited in each corner of the rocky mass (Figure 2).

From this non-exhaustive literature review and our traditional field observations, we can propose some assumptions to elucidate the main extrinsic and intrinsic weathering factors of Madâin Sâlih sandstones and to conduct this study:

- No biodeterioration of sandstone surfaces was observed and the average in the precipitation is about 16 mm, insufficient quantity to provide salt dissolution and crystallization.
- The amount of loose sand by product of weathering and the presence of sand dunes throughout the near North and North-East is remarkable suggesting that weathering under wind-blown sand environment is probably the main factor for Madâin Sâlih site degradation. Besides, the matrix of the rocks is still unknown until today.

This paper aims to provide new contribution necessary to clarify and to identify the important weathering factor of Qasr al Bint in Madâin Sâlih and to explore the archeological area.

In order to achieve this goal, we present at first a comparative study of some physical properties of sand samples from the rock and the rocky mass. Second, we report the chemical composition (mineralogical) analysis of the rock to determine the nature of the cement agent.

2. Materials and methods

2.1. Sample area and sampling

As it can be seen from Figure 2(b) that the shifting sand has been deposited surrounding the site in different amounts depending on the wind direction. Regional wind may be responsible for the removal of the weathering produced sand.

For experiment, we have selected five points from the study area for sampling (Figure 3). These samples designated as sample from the south direction (SS), sample from the north (SN), sample from the west (SW), sample from the east (SE) and rocky sample (SR) according to their sampling position.

2.2. Analytical methods

From each point, 200 g of sand were collected and dry-sieved to perform a granulometric analysis using ASTM standard sieves. This sieve analysis involves a nested column of sieves with different wires mesh each lower sieve placed in the column has smaller openings than the above one. We have used a column of five sieves with limits 40–100 µm, 100–200 µm, 250–300 µm and 300–500 µm respectively. Then, each

| Sample | Sieve opening (µm) | Specific gravity (g/cm³) |
|--------|--------------------|--------------------------|
| SR < 40 | Pass through 40    | 2.93                     |
| SR     | Retained in 300–500 | 2.77                     |
| SE     | Retained in 300–500 | 2.75                     |
| SN     | Retained in 300–500 | 2.64                     |
| SW     | Retained in 300–500 | 2.66                     |
| SS     | Retained in 300–500 | 2.69                     |

Figure 5. Particle size distributions of sand samples studied.
A sample was divided into six fractions. After the mechanical shaking, the amount of sand of each sieve is weighed and the retained percentage is calculated relatively to the total weight:

\[
\text{Retained \%} = \frac{W_{\text{Sieve}}}{W_{\text{Total}}} \times 100, \quad (1)
\]

where \(W_{\text{Sieve}}\) is the weight of sand in the sieve and \(W_{\text{Total}}\) is the total weight of the sample (200 g).

As it can be seen from Figure 4, the representative fraction is the one retained between the sieves 300 and 500 µm. It can be seen that sand samples are similar in being unimodal with a modal class in the size fraction (300–500 µm). In the next, only this fraction will be considered for all samples SS, SN, SW, SE and SR. The fine fraction issue from SR (noted SR < 40) was used to determine the type of cement agent.

Specific gravities were determined using water pycnometer according to ASTM D854 [18] description. Identification of each sample composition was conducted by XRD carried out using a Phillips diffractometer (35 kV, 20 mA) with CoK\(_\alpha\) radiation and a graphite monochromator on a diffraction range 5–80°. Their morphologies were investigated by scanning electron microscopy (SEM); an energy dispersive spectroscopy (EDS) unit was attached for elemental analysis. The EDS detector is equipped with an ultra-thin window allowing detection of mineral elements and carbon. Before analysis, each sample was coated with carbon to avoid charges. Additionally, to identify the nature of cemented agent specially in the finest fraction, Fourier Transform Infrared (FTIR) spectra in the region 4000–200 cm\(^{-1}\) were investigated using Thermo Scientific spectrometer with DTGS detector and a KBr splitter. The KBr pressed disc technique (1 mg of sample in 200 mg of KBr) was used. Spectra manipulations were performed using the OMNIC software package (Thermo Instruments Corp).

Figure 6. XRD diffractograms.

Figure 7. FT-IR graph of sample SR < 40.
3. Results and discussion

3.1. Grain size distribution analysis and specific gravity

For all examples we have calculated the mean diameter according to the formula:

$$d_m = \frac{\sum_{i=1}^{n} W_i d_i}{\sum_{i=1}^{n} W_i}, \quad (2)$$

where $d_m$ is the mean diameter, $W_i$ is the sample weight and $d_i$ is calculated by:

$$d_i = \frac{d_{\text{max}} - d_{\text{min}}}{2}. \quad (3)$$

The values of $d_m$ were 336.32 μm for SR sample and 322.17; 283.91; 303.21 and 319.62 μm for SE, SN, SW and SS respectively. Studying sedimentological, mineralogical and geochemical characterization of sand dunes...
in Saudi Arabia, Benaafi and Abdullatif [19] reported that sand dunes from Tayma area (Not so far from Madâin Sâlih archeological area) showed the coarse mean grain size, the mean diameter is 250–350 μm. In Figure 5, we plotted on the y axis the cumulative percent passing and on the x axis the logarithmic sieve size. Examination of Figure 5 indicates that all samples have the same grading characteristics and the sands RS and ES have a fines content of about 6%.

Also, we have determined the specific gravity for the chosen fraction for all samples our results are summarized in Table 1. The specific gravity varies between 2.64 and 2.77 μm. Such values are in agreement with those published by Al-Sanad et al. [20] for the dune sands of Arabian Peninsula (varies between 2.62 and 2.75 g/cm³). The differences observed between the samples from the rock (SR < 40 and SR retained on a 300–500 μm mesh sieves) are probably due to their chemical compositions.
X-ray diffractograms (Figure 6) indicate the characteristic peaks of quartz prevailing at 4.22 and 3.34 Å and the characteristic peaks of Kaolinite (k) prevailing at 7.1 Å and 3.55 Å. Furthermore, XRD analysis revealed no peak below $2\theta = 10^\circ$ characteristic of expansive clay (Montmorillonite, illite). The peak at 1.66 Å (hkl 211) is attributed to the rutile. From this figure, we concluded also that there are no observed diffractions at $2\theta$: 11.69°, 23.45° and 29.19° due to gypsum (CaSO$_4$·2H$_2$O), contrary to Mechri et al. [21] results, who found gypsum in their sand sample. According to Paradise [3], the effect of solar flux, as a factor of rock weathering, is more pronounced on a rock with calcium content more than 10% due to the well-known phenomenon expansion/contraction of calcite crystal. In this figure no peak for calcite was observed. So the solar flux is not a meaningful parameter in the degradation of rocks in Madain Saleh.

The infrared absorption spectrum gives information about the nature of chemical bonds that exist in the material. We have used this technique to identify the nature of clay used as binding agent for sand particle in the rock.

Figure 7 shows the FTIR diagram of the fine fraction SR < 40. The part (a) in this figure noted the fingerprint region of the infrared spectra for Kaolinite [22]. From this figure, we noted the three well-known characteristic bands in clay around 1100, 1040 and 1031 cm$^{-1}$ arises from the asymmetric Si–O–Si stretching vibration of Kaolinite. The IR absorption band around 911 cm$^{-1}$ is due to Al(OH) vibrations in octahedral site. Typical Si–O band of silica is observed at 794 cm$^{-1}$ [23]. The hematite (presence of Fe) is identified by the presence of the IR band around 353 cm$^{-1}$ [22]. According to our FT-IR study, no peak characteristic of calcite (875 and 712 cm$^{-1}$) [23] was observed.

EDS analysis shows that Si, Al, Fe, Ca, Mg and K are with high concentrations across SR < 40 and SR 300–500 particles. This elemental composition is similar to that observed for clays [24]. On the other hand, our EDS analysis reveals that Si element is the main component across the other samples (Figure 8(a–f)).

As it can be seen from the above figure, the fine fraction (SR < 40) is composed with platelets and fine angular to sub-angular particles (Figure 9(a)). SR fraction is constituted with coarse sand particles showing deposition on the surface (Figure 9(b)). SW and SE show irregular angular shape sand particles as it can be observed from Figure 9(c, f). On the other hand, SE and SN exhibit large grains with more fractured portions (Figure 9(d, e)). According to Krinsley and Smith, [25] this morphology reminisces that of the aeolian sand.

4. Conclusion

This study deals with weathering on sandstone in Qasr Al Bint at Madâin Sâlih archeological area Northwest Saudi Arabia under wind-blown sand environment. One sand sample from the monument and other samples from four orientations were investigated using different analytical techniques (Grain, size distribution, XRD, FT-IR and SEM/EDS).

The obtained results demonstrate clearly that:

- Sandstones at this site are clay-cemented sandstones.
- Clay is Kaolinite, non-swelling type, will not hold water to promote salt weathering or tafoni development.
- Mean annual precipitation at Madâin Sâlih is about 16 mm and under these conditions biodeterioration may not be considered as the primary weathering factor.
• Change in sandstone colour is due to the oxidation of iron (confirmed by EDS analysis).
• Morphological characteristics of sand sample from the monument are different from those of shifting sand samples.
• SN and SS grains are more rounded edges than SE and SW particles which are angular.

From these conclusions and our field observations, we believe that wind-blown sand is the meaningful weathering factor in Madâin Sâlih. Ongoing research we focus on the study the effect of solar flux and the quantification of the rate of sandstone damage under insolation and sandstorm.

Acknowledgements
The authors wish to thank the Deanship of Scientific Research of Taibah University, Al-Madinah Al-Munawarah, K.S.A for financial grant support No (6281/1436) of this research. The authors are also deeply indebted to the team of the Deanship of Scientific Research of Taibah University for their continuous help to achieve this work. Dr N.MEKNI for spectroscopy analysis help.

Disclosure statement
No potential conflict of interest was reported by the authors.

References
[1] Fitzner B, Heinrichs K. Damage diagnosis on stone monuments-weathering forms, damage categories and damage indices. In: Pirkryl R, Viles HA, editor. Understanding and managing stone decay. Prague: The Karolinum Press; 2002. p. 11–56.
[2] Paradise TR. Sandstone architectural deterioration in Petra Jordan, 9th international congress on deterioration and conservation of stone. Venise; 2000, 19–24.
[3] Paradise TR. Sandstone weathering thresholds in Petra, Jordan. Phys Geogr. 1995;16:205–222.
[4] Zhang Z, Yang Z, Wang S, et al. Weathering rates of a sandstone structure in a semi arid environment: A case study of the ancient city of Pingyao (world cultural heritage), China. Bull Eng Geol Environ. 2011;70:231–237.
[5] Paradise TR. Assessment of tafoni distribution and environmental factors on a sandstone djinn block above Petra, Jordan. Appl Geogr. 2013;42:176–185.
[6] de la Rosa JPM, Porcel MC, Warke PA. Mapping stone surface temperature fluctuations: implications for lichen distribution and biomineralization on historic stone surfaces. J Cult Herit. 2013;14:346–353.
[7] Pope GA, Meierding TC, Paradise TR. Geomorphology’s role in the study of weathering of cultural stone. Geomorphology. 2013;47:211–225.
[8] Waragai T. The effect of rock strength on the weathering rates of sandstone used for Angkor temples in Cambodia. Eng Geol. 2016;207:24–35.
[9] Benito G, Machado MJ, Sancho C. Sandstone weathering processes damaging prehistoric rock paintings at the Albarracín cultural park, NE Spain. Environ Geol. 1993;22:71–79.
[10] Goudie AS, Wright E, Viles HA. The role of salt (sodium nitrate) and fog in weathering: A laboratory simulation of conditions in the northern Atacama Desert, Chile. Catena. 2002;48:255–266.
[11] Fitzner B, Heinrichs K, La Bouchardiere D. Weathering damage on pharaonic sandstone monuments in Luxor-Egypt. Build Environ 2003;38:1089–1103.
[12] Bani-Hani K, Barakat S. Analytical evaluation of repair and strengthening measures of Qasr al-Bint historical monument – Petra, Jordan. Eng Struct. 2006;28:1355–1366.
[13] Hosono T, Uchida E, Suda C, et al. Salt weathering of sandstone at the Angkor monuments, Cambodia: Identification of the origins of salts using sulfur and strontium isotopes. J Archeol Sci. 2006;33:1541–1551.
[14] M.M. Abd El-Hady, The deterioration of Nubian sandstone blocks in the ptolemaic temples in Upper Egypt. In: Proceeding of the 9th International Congress on Deterioration and Conservation of Stone. Venice June 19–24, Elsevier 2 (2000) 783–792, Amsterdam.
[15] Temraz MG, Khalaf KM. Weathering behavior investigations and treatment of Kom Ombo temple sandstone, Egypt-based on their sedimentological and petrographical information. J Afr Earth Sci. 2016;113:194–204.
[16] Cardoso OR, Balaban RC. Comparative study between botucatu and berea sandstone properties. J S Am Earth Sci. 2015;62:58–69.
[17] Vincent P, Sadah A. Particle size spectra of some Saudi Arabian pedosediments. J Arid Environ. 1996;33:1–8.
[18] ASTM D 854, Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer. Annual Book of ASTM Standards. American Society for Testing and Materials, West Conshohocken, PA. 2010.
[19] Benaafi M, Abdullatif O. Sedimentological, mineralogical and geochemical characterization of sand dunes in Saudi Arabia. Arab J Geosci. 2015;8:11073–11092.
[20] Al-Sanad HA, Ismael NF, Nayfeh AJ. Geotechnical properties of dune sands in Kuwait. Eng Geol. 1993;34:445–52.
[21] Mechri ML, Chishi S, Mahdadi N, et al. Study of heat effect on the composition of dunes sands of Ouargla (Algeria) using XRD and FTIR. Silicon. 2016;4:69–79.
[22] Singh P, Sharma S. Thermal and spectroscopic characterization of archeological pottery from Ambri, Assam. J Archeol Sci Rep. 2016;5:557–563.
[23] Reig FB, Adelantado JVG, Moreno MCM. FTIR quantitations and treatment of Kom Ombo temple sandstone, Egypt-based on their sedimentological and petrographical information. J Afr Earth Sci. 2016;5:557–563.
[24] Vortisch W, Harding D, Morgan J. Petrographic analysis using cathodoluminescence microscopy with simultaneous energy-dispersive X-ray spectroscopy. Miner Petrolog. 2003;79:193–202.
[25] Krinsley DH, Smith DB. A selective SEM study of grains from the Permian yellow sands of north-east England. Proc Geol Assoc. 1981;92:189–196.