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IR AND ED-XRF ANALYSIS OF CHRISTIAN PLASTER AND MORTAR FROM SITE MRB-05-001 AT EL GA'AB DEPRESSION, WESTERN DONGOLA

INTRODUCTION

Analytical chemistry has been used to address questions that do not relate directly to archaeological interpretation, but which nevertheless have importance for understanding the processes that act upon the archaeological record and the materials within it. Applied chemistry and physical methods in archaeology has a long history dating back to mid eighteenth century, and relied extensively on the contributions of great scientists such as Martin Heinrich Klaproth (1743–1817), and it is gratifying to see how many of these pioneers considered archaeological material as a suitable subject for study. The important reason for the chemical and physical analysis in archaeology is to answer the simplest archaeological question “what is this object made from?” During the 1960s an air path machine was developed in Oxford specifically to allow the nondestructive analysis of larger museum objects (Hall 1960), and since then a portable hand-held XRF system has been produced for use on museum displays or at an archaeological excavation, as well as for geological purposes (Williams-Thorpe *et al.* 1999).

The earliest analytical test that we know of is a measure of the purity of gold, which was certainly in use by the third millennium BC in the Near East (Oddy 1983). The simplest method of XRD analysis, used in early studies and described by Tite (1972: 286), is the powder diffraction method. In archaeology, the main application of EDXRF is for rapid identification and semiquantitative analysis of a wide range of materials including metals and their alloys, plaster, ceramics, glass, jet, faience, pigments, glazes, gemstones, and industrial debris. The key characteristic of XRD is its ability to identify crystalline minerals. The primary use of the powder XRD method has been the identification of clay minerals in pottery in order to characterize pottery types and

to investigate sources for raw materials (Pollard *et al.* 2007).

In chemistry, infrared spectroscopy is usually the first method of choice for the identification of organic and inorganic functional groups. Fourier-transform infrared (FTIR) spectroscopy is considered to be one of the most appropriate experimental techniques for the analysis and the characterization of molecular composition in the field of material science and cultural heritage. Even in small amounts, the minerals present in ceramics or in art objects are easily identifiable, and can provide useful information on the provenance of raw materials such as clays or pigments (Griffith, 1987; Shoval, 2003; Shoval and Beck 2005; Sodo *et al.* 2003).

The value of infrared spectroscopy in archaeology and materials conservation has been greatly enhanced in the last ten years or so by the development of infrared microscopes (Kempfert *et al.* 2001). When using laser illumination and Fourier transform detection, these microscopes are capable of recording the IR spectrum. Fourier transform infrared microscopy offers a versatile analytical tool, which is fast and easy to use, and in which sample preparation is minimal or unnecessary for characterizing micro- and macro-samples (Pollard *et al.* 2007).

XRF spectrometers are generally designed for the analysis of solid samples, preferably of a standard shape (usually a disk) and mounted flat in a sample holder. It is widely used in industrial applications where a large number of elements need to be determined quantitatively (Pollard *et al.* 2007).

Energy Dispersive X-ray Fluorescence (EDXRF) technology provides one of the simplest, most accurate and most economical analytical methods for the determination of the chemical composition of many types of materials. It can be used for a wide range of elements, from sodium (11) to uranium (92), and provides detection limits at the sub-ppm level; it can also measure concentrations of up to 100% easily and simultaneously (Clapera 2006: 25).

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There have been many analytical methods applied in Sudanese Archaeology. Khabir (Khabir 1987) presented the results of petrographic and XRD analysis of a series of pottery and clay samples from site Sarurab-II on the west bank of the Nile about 30 km north Omdurman. The petrological analyses show that the mineral inclusions of the pottery are present in the natural clay of the area, although none of the clay samples matched the pottery exactly. X-ray diffraction analysis of pottery showed that quartz was the most important mineral constituent in the clay, and the pottery and clay samples were chemically similar. Hence it is likely that the pottery was made from the same type of clay.

Bouchar (2010) studied Meroitic mortars from the Amun temple in el-Hassa, using X-ray diffraction, X-ray fluorescence, and mercury intrusion porosimetry. The application of a methodology that cross-referenced the data obtained by all analytical techniques indicated that the paste was probably made of a mixture of both lime and a material comprising gypsum and limestone grains.

Letourneux and Feneuille (2010) presented XRD, XRF and porosimetry analyses alongside SEMEDX observations of nine mortars: three Egyptian plasters (New Kingdom, 15th - 11th century BC) and six Meroitic mortars (1st century AD) collected from temples, palace and pyramids from archaeological sites located between the Third and Fourth Cataracts. The first two Egyptian samples were mainly composed of gypsum plaster. The third one and a binding mortar collected from a Meroitic pyramid were composed of siliceous sand bound by about 30% kaolinite-rich clay.

Khabir (2014) presented the XRD and XRF analysis of pottery samples from site Islang 2 and Nofalab 2. The results showed that the pottery and modern clay samples were comparable. An explanation for this may be that the sources of temper (Nubian sandstone and basement complex) and raw material (Nile silt and alluvial clay) were rather homogenous.

During the conservation of the Amun temple at Dangeil, Sweek (et al 2014) used a Centaurus back-scattered electron detector in a Hitachi S-3700N variable pressure scanning microscopy (VP-SEM:20 kv 30 Pa) and Energy dispersive X-ray (EDX) was used in their research, and microanalysis was conducted on all uncoated cross sections to analyse and map their elemental compositions. Scientific analyses have shown that the purchase of good quality lime is essential for the success of the capping (Sweek et al 2014).

Hamdeen (2016) presented the results of chemical analysis of four Meroitic plaster samples collected from the Amun Temple and Royal Bath in the Royal City of Meroe. The analysis was carried out according to “IS 1727 (1967) *Indian Standard methods of test for pozzolanic materials*³”. The results indicated that all chemical constituents of natural pozzolanic materials were present in these samples, which suggests that the use of plaster in the Meroitic civilization depended on the function of buildings for example the plaster that was used in the Royal Bath, basins and the other water building is different from that was used in the Amun temple, palace and other non-water buildings.

THE EL GA'AB DEPRESSION

The El Ga'ab depression is situated south of the Third Cataract of the Nile on the west bank, at the northern end of Dongola Region. It extends about 123 km, crossing the desert in a south-western direction. It diverges from the Nile southwards; the nearest point to the river is about 6 km at the northern tip and the furthest point at 60 km in the southern part. Its width varies from 2 to 8 km. The lowest portion of the wadi El Ga'ab must be considerably lower than the level of the river flood (214 m above sea level) (Tahir 2012). The area can be divided into 3 regions (see Map 1):

1- *The northern channel*

This is a narrow channel, with a gravel-covered mouth in the north. It begins in the vicinity of Soroog Village (19°45' 517 N/30°23' 120 E), running from the terrace soil westwards to the desert (6 km). Most areas of this channel are covered with gravel. Sporadic irrigation wells (Mutras) were found, but no human habitation or settlement.

2- *Wadi El Hashsha*

The channel expands and is filled with terrace and alluvial soils. This area is called Wadi El Haahsha Bahri (north). South of this wadi at the constriction of Jebel El Hasha (west) and rocky mounds (east), Wadi El Haahsha Gobli (South) follows southwards. A large number of Mutras were seen in these agricultural lands. Despite this, very little human habitation is known there.

3 IS-1727, 1967 Method of test for pozzolanic materials Bur. Indian Stand. New Delhi.

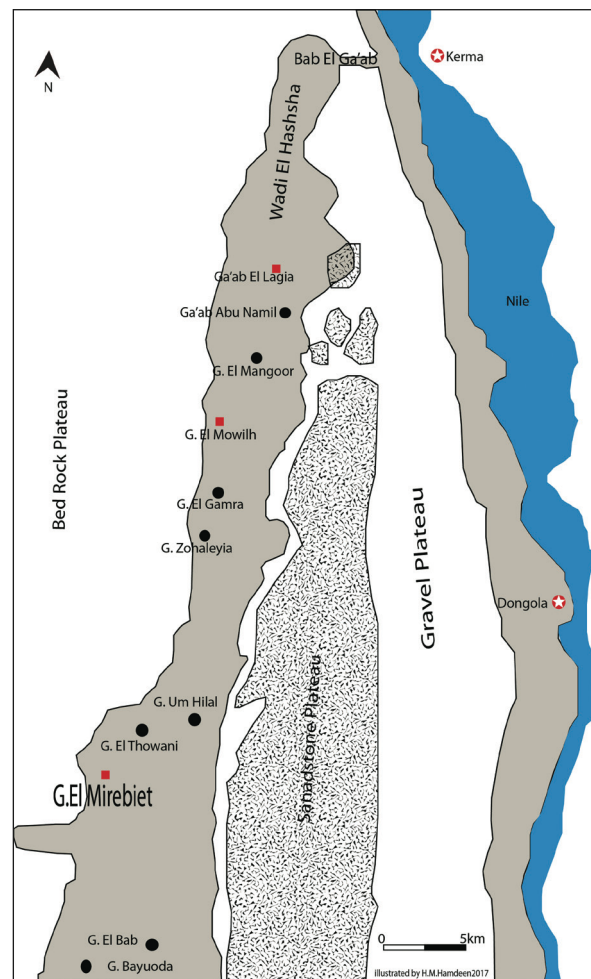


3- Ga'abs (Oasis)

To the south of the Wadi Hashsha there is a series of Ga'abs, where villages and hamlets for human settlement are found. The largest Oasis is Ga'ab El Lagia in the north. Others are Ga'ab Abu Namel, Ga'ab Um Hilal, Ga'ab El Thowani, Ga'ab El Bab, Ga'ab Guma'a, Ga'ab Byoda and Ga'ab Bauoda.

SITE MRB- 05-001

The site is located at Ga'ab El Meribiet to the southwest of Ga'ab El-Thowani in the El Ga'ab depression. It is 16 m east-west and 12 m north-south and it is covered with sand in most parts. The wall thicknesses vary: the northern wall thickness is 70 cm, the southern wall is 65 cm, the eastern wall is 49 cm, and the western wall is 60 cm. It consists of a building (possibly an altar that is cross-like) on the top of which there is a square basin. The building also contained an eastern corridor (partition) near the basin in the centre, two rooms (halls) in the southwest and the northwest, two hallways and a doorway in the south (Fig. 1). On the site surface, there are coloured pottery sherds of different shapes, upper grinding tools, carbon, and animal bones. According to preliminary studies on archaeological data from site MRB-05-001, the ceramic can be dated to middle and late Christian period, and the function of the site was connected to wine manufacturing, because



Map 1: The location of El Ga'ab Depression.

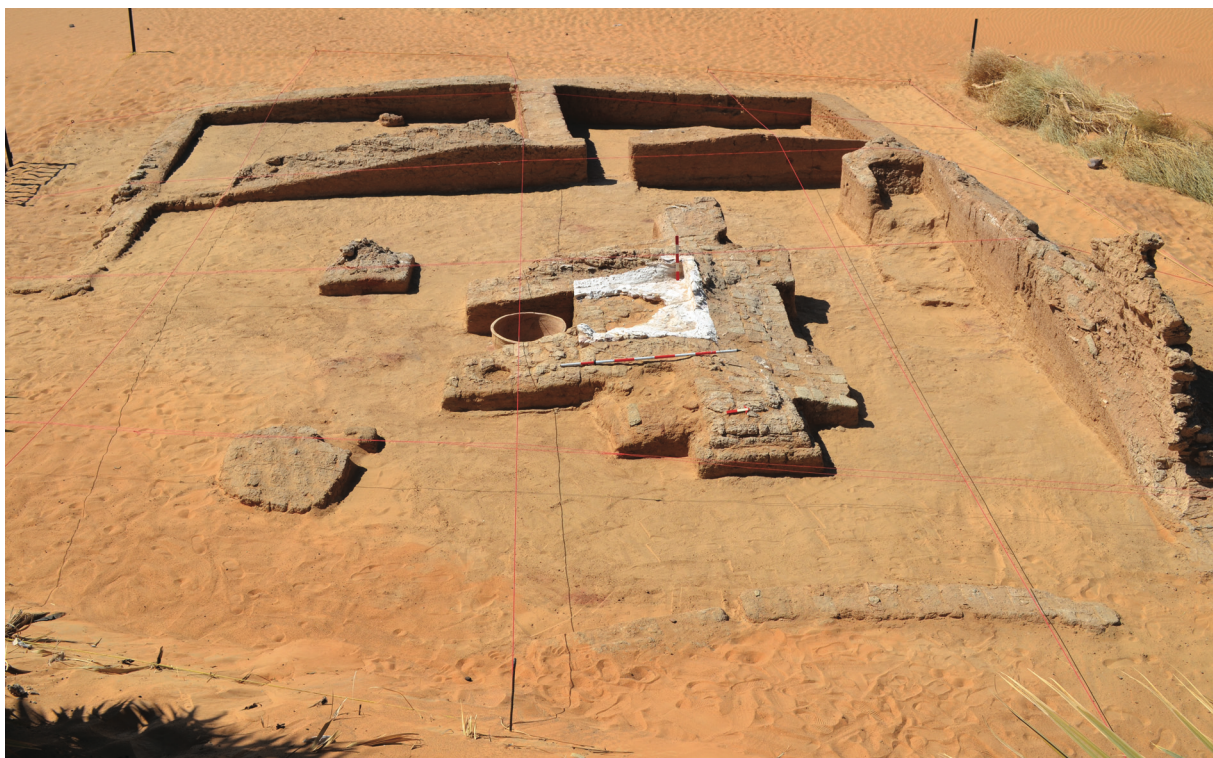


Fig. 1: General view of the site MRB-05-001.

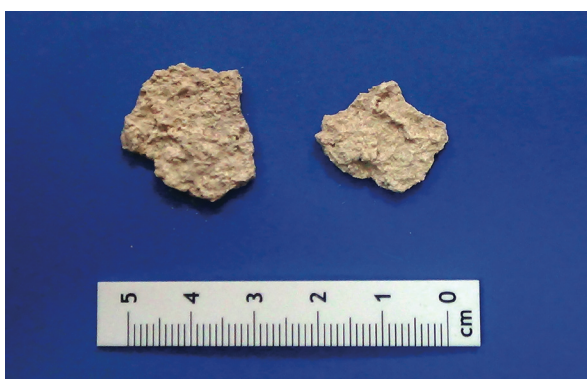


Fig. 2: The basin building and sample at site MRB-05-001.

these types of the buildings were known in Sudan generally and specifically from the Third Cataract (Said and Tahir 2016).

MATERIALS AND METHODS

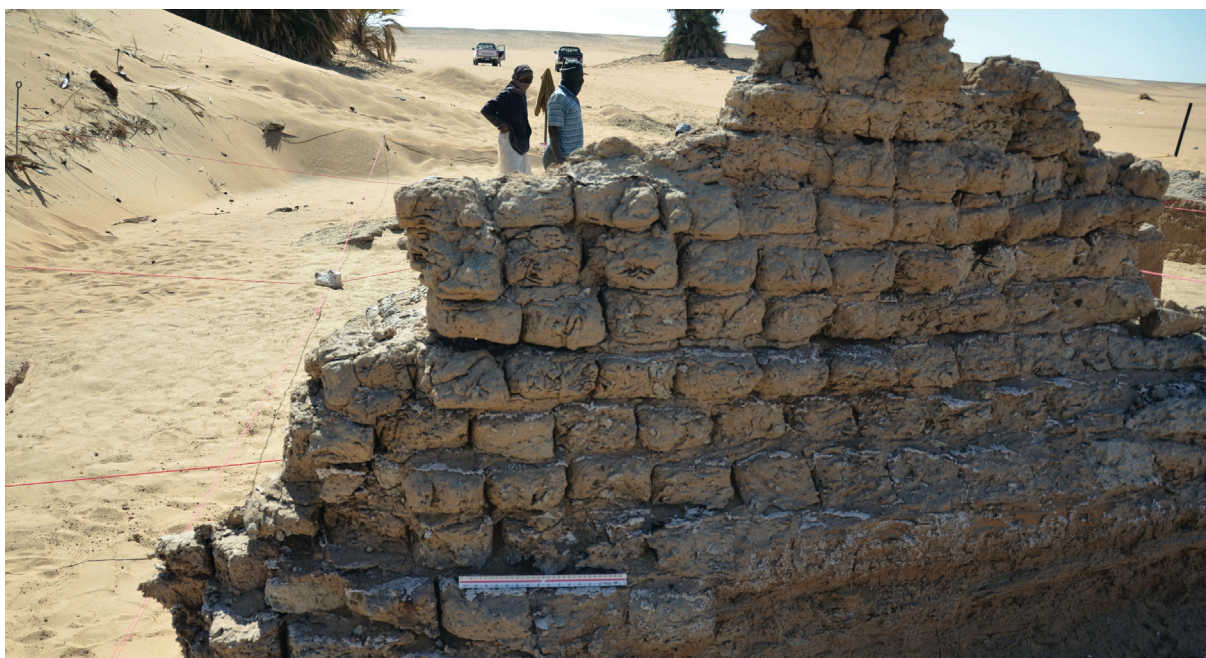
The research question for this paper concerns the chemical elements contained in the mortar and plaster of the site MRB-05-001. For that twelve samples were collected for analysis. Two archaeological samples were taken, one from the plaster in the basin building and the other from building mortar in the northern wall (Figs. 2 and 3) at site MRB-05-001. To gain knowledge about the source of the raw materials for mortar and plaster the other ten samples were collected from playa sediments (Fig. 4 and cover picture) in Ga'abs: Kogil, Lagiya, Meribiet, El Bab, Baoda, Mowlih, Zohiliya, Um Hilal and Thowani (see Map 1).

Fourier Transform Infrared Spectrophotometer

The infrared spectra of powders were recorded using a FTIR 8400S Shimadzu (Japan). KBr pellets were prepared to obtain spectra of the samples, in the spectral range between 4000 and 400 cm^{-1} , with 4 cm^{-1} resolutions.

Energy dispersive – X-ray Fluorescence

The samples were ground down to a powder by mortar and pestle, then 1 gram was pressed into 2 cm^2 circular disk. The X-ray isotopic source was used



to measure the samples utilizing ^{109}Cd which has regular energy 22.6 Kev. Si(Li) detector, the CAN-BERRA amplifier model 2020 was set up with a high voltage supply of 600 V.

RESULTS AND DISCUSSION

Fourier-transformed infrared (FTIR) characterization allowed the identification of distinctive vibrational features that have been correlated to the presence of specific compounds. By comparing the observed wavelength with the available literature, the different types of inclusions in the two samples (Figs. 5 and 6) and the playa samples were identified.

Considering the chemical aspects of the FTIR analyses, the bands between 1427 cm^{-1} are carbonated, mainly of calcite (CaCO_3) and dolomite [$\text{CaMg}(\text{CO}_3)_2$] (Seetha and Velraj 2015; Shoval and Beck 2005). The bands between 999 cm^{-1} and 1014 cm^{-1} , and also 428 cm^{-1} are assigned to feldspar, plagioclase and clay minerals which are identified as orthoclase/microcline ($\text{KAlSi}_3\text{O}_8/\text{KAlSi}_3\text{O}_8$), oligoclase [$(\text{Na,Ca})(\text{Si,Al})_4\text{O}_8$] and kaolinite/illite [$(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)/[(\text{K,H}_3\text{O})\text{Al}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2]$, respectively (Farmer and Russell 1964; De Benedetto *et al.* 2002; Ravisankar *et al.* 2011).

Furthermore, the band at 873 cm^{-1} which is seen in the majority of the samples (except for the two archaeological samples) also indicates the presence of pyroxenes (diopside [$\text{Ca}(\text{Mg,Al})(\text{Si,Al})_2\text{O}_6$]/augite [$\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$]) (Maritan *et al.* 2006) characterised by a high heating rate and short residence time in a reducing atmosphere; kiln firing, with a low heating

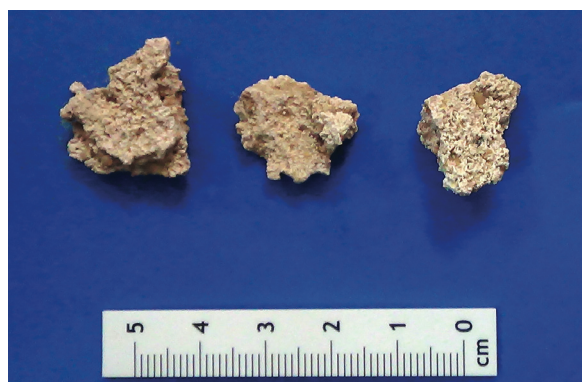
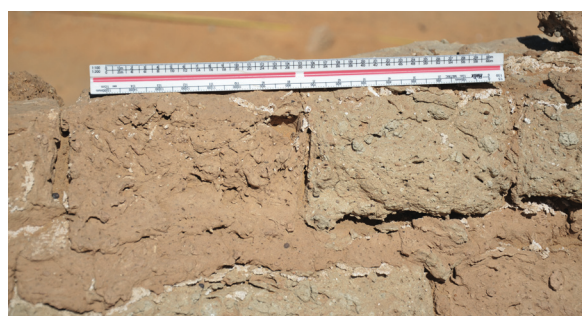
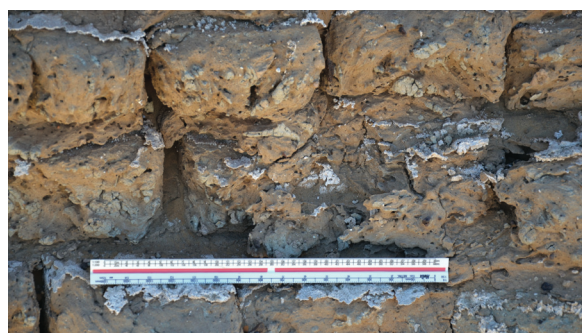


Fig. 3: Building mortar in the northern wall and sample at site MRB-05-001.



Fig. 4: Playa sediments in Ga'ab El Bab.

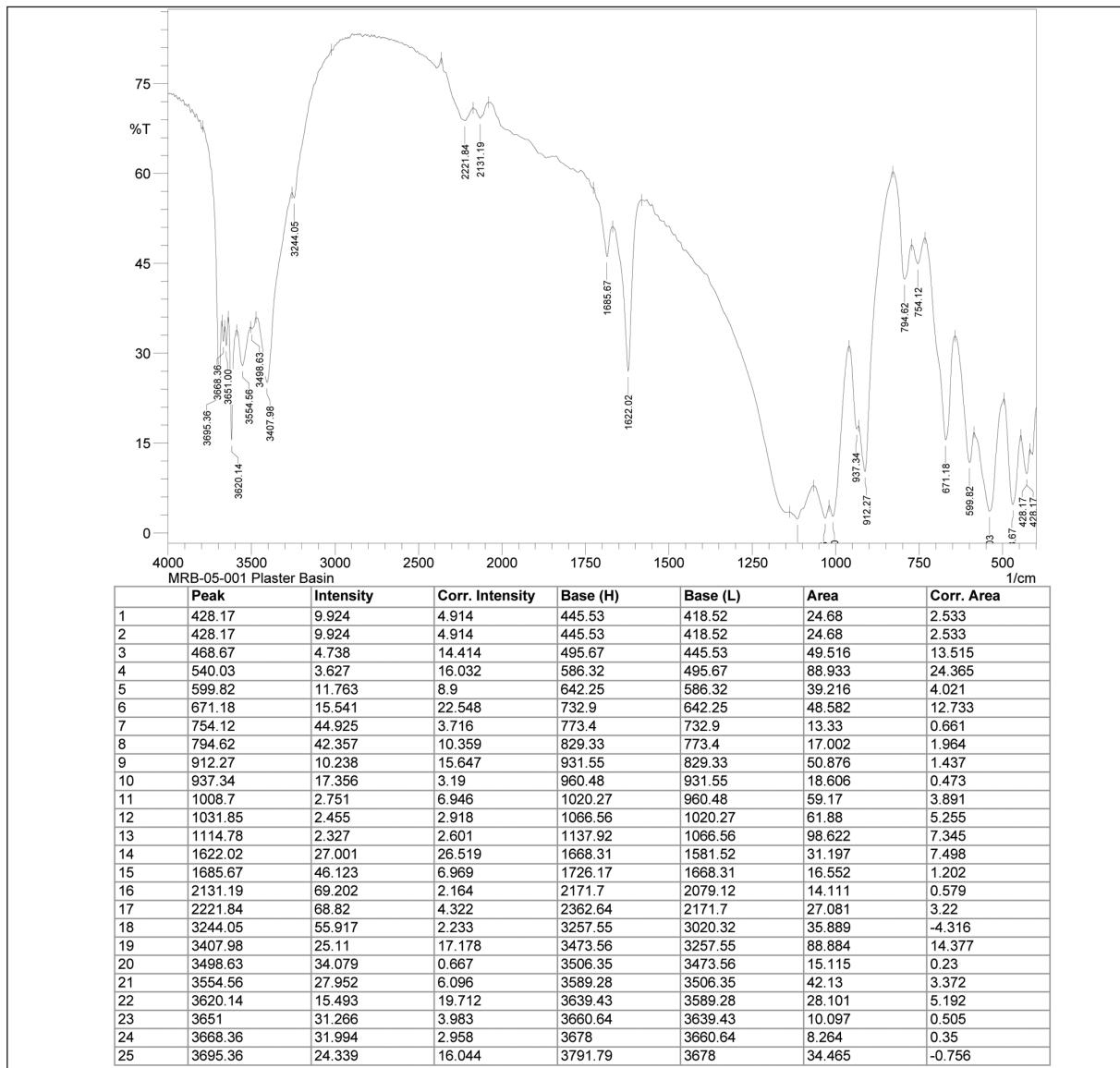


Fig. 5: The results of FTIR wavelengths of plaster basin sample from site MRB-05-001.

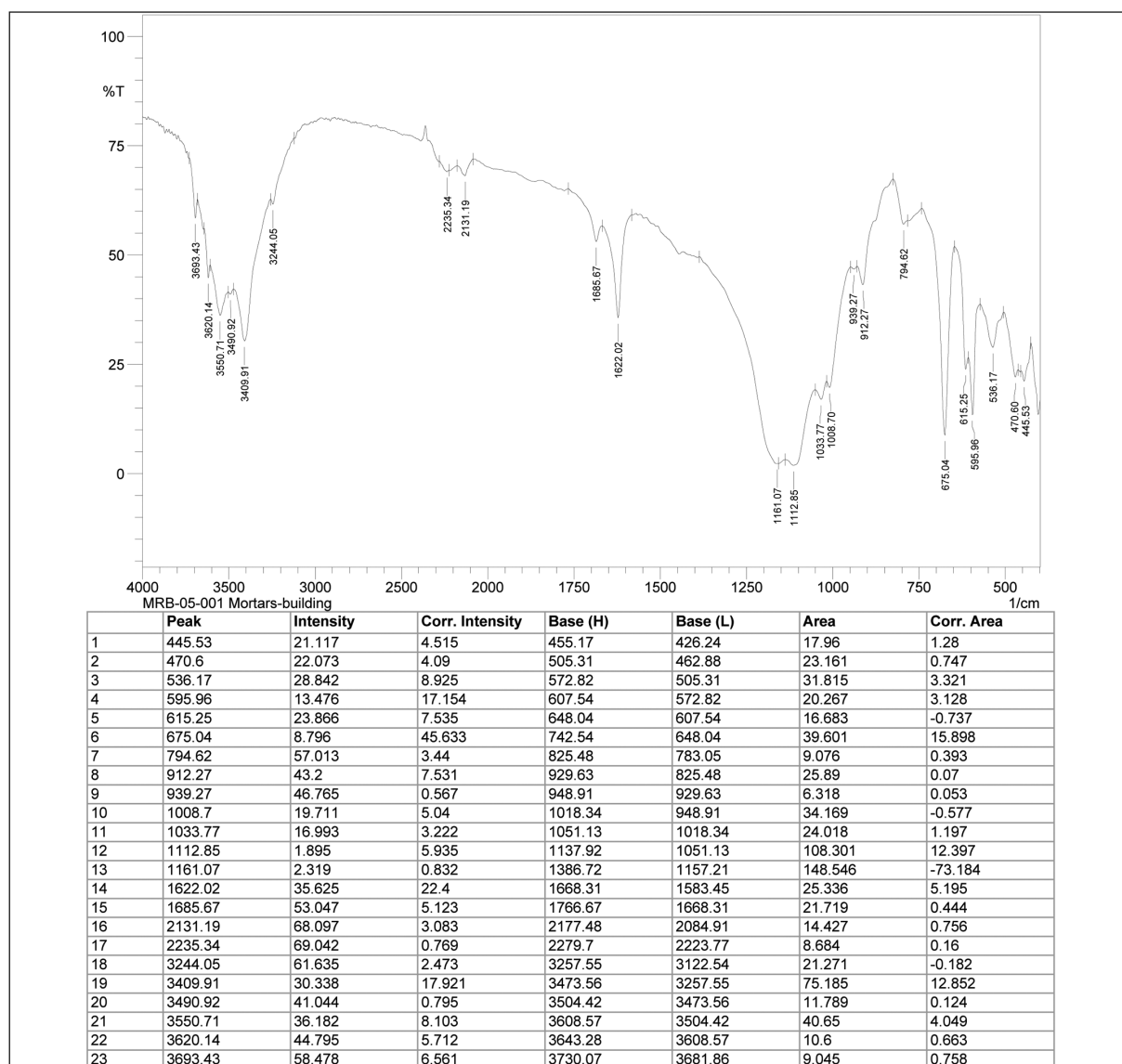


Fig. 6: The results of FTIR wavelengths of mortar-building sample from site MRB-05-001.

rate and long residence time in an oxidising atmosphere. As expected, pit firing conditions produced uniformly reduced ceramics, and gehlenite, diopside and spinel occurred at suitable temperatures (above 900 °C). The band at 468 cm⁻¹ also indicates an Si-O-Si deformation band of clays and may suggest the breakdown of the elite structure (Hall and Minyaev 2002). The kaolin spectra show four bands, at 3697, 3669, 3645 and 3620 cm⁻¹, and these characteristic bands are observed in the samples. The wavelengths at around 3620 cm⁻¹ has been assigned to the inner hydroxyls, and the wavelengths observed at around the other three predictable bands are predominantly ascribed to vibrations of the external hydroxyls (Schroeder 2002). Weak peaks around 912 and 880 cm⁻¹ correspond with C-C-H stretching and bending modes, respectively. Further investigation showed a better match to all samples except the

samples from (Kogil Playa 2). The characteristic haematite peak is represented around 535 cm⁻¹.

The two samples from the basin and mortar at site MRB-05-001 is a lime plaster containing some selected quartz filler. The plaster contained calcite, gypsum, silicates and ferrous material as main elements of the sample with an addition of titanium. The considerable presence of silicates is presumably due to an addition of clay or silt. These results from IR agree in some aspects with the results of the analysis of plaster from the cruciform building (B.III) in Old Dongola (Koss 2003), especially the presence of calcite, silicate, quartz and ferric compounds and this indicates a relationship in the development of plaster techniques between the El Ga'ab and Old Dongola.

The spectra of IR analyses indicates there are close similarities in the IR spectra between the two archaeological samples of building mortar and the

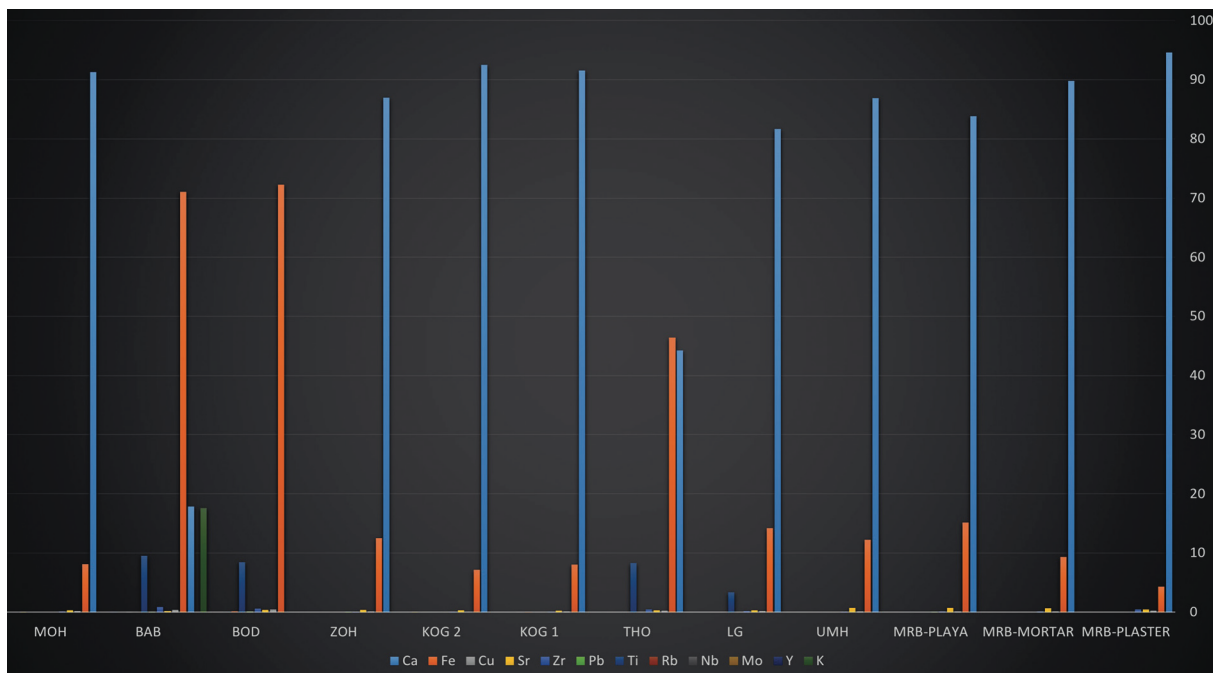


Fig. 7: The results of X-Ray Florescence the elemental composition.

plaster basin with that of MRB playa. These results indicate that the plaster and mortars were made from the same type of playa materials that were collected from Ga'ab El Meribet area.

The results of X-Ray Florescence showing the elemental composition of the two ancient building mortars, the plaster basin and the rest of the reference samples were performed by using ED-XRF spectroscopy, as shown in fig. 7. The results demonstrate a close similarity between the archaeological samples and MRB, MOH and LG playa.

Energy dispersive X-ray fluorescence (ED-XRF) was used to determine the minor and trace element composition of plaster and mortars from El Ga'ab. We can conclude that the concentrations of the same elements in archaeological and MRB, MOH and KOG1 playa samples, indicate that the plaster and mortars were made from the same type of playa material from the Ga'ab El Meribet, Mowalib and Kogil areas. The difference in chemical composition in the basin plasters may be the result of their different functions. This is the same to the material from Meroe, as the plaster used in the Royal Bath and basins needed to resist cracks and water infiltration, while this was not necessary in the Amun temple and palaces (Hamdeen 2016). The XRF results show that the most abundant elements were Ca, Fe, K, and Ti. The composition of Fe and Ca determines the nature of clay minerals and the firing atmosphere adopted by the artisans during the Christian period in the El Ga'ab depression.

CONCLUSIONS

The similarity between the two archaeological samples, mortar sample from the northern wall and basin plaster sample at site MRB-05-001, and playa samples from three areas (MRB, MOH and KOG1), indicate that the plaster and mortars were made from the same type of playa materials from the three areas. This indicates a relationship between the three Christian complexes in El Ga'ab depression: The same plaster was found in the three Christian complexes of Lagia church, El Hamra church in Ga'ab Mowlih and site MRB-05-001 in El Merabeit. The differences in the chemical composition of the basin plaster, when compared with that of the mortars and playas, is probably functional (Hamdeen 2016). The IR and XRF analyses of archaeological samples from site MRB-05-001 provide further information about the chemical composition of building materials and new evidence for the study of ancient building techniques during the Christian period from the desert western Dongola. When we compare the plaster material from the El Ga'ab area (Ga'ab El Mirebiet and El Lagiya) in the desert with other plasters at the Nile, we can observe some similarities which could suggest a cultural relationship between El Ga'ab and Old Dongola during the early, middle and late Christian periods.



ACKNOWLEDGMENT

The project is very grateful for the funding provided by the Qatar-Sudan Archaeological Project which made its activities possible, and the NCAM for give us the concession area. Our thanks also go to the el-Ga'ab mission members, and Fatima El Bashir for the analysis of the samples, and our drivers Mudather Abdelhameed and El Nour Ahmed.

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ZUSAMMENFASSUNG

In diesem Beitrag werden die Ergebnisse der IR- und ED-XRF-Analyse von Gips und Mörtel der christlichen Zeit aus dem site MRB-05-001 in der El Ga'ab-Senke vorgestellt. Um zu erfahren, welche chemischen Elemente im Mörtel und Gips dieser Stätte enthalten sind, wurden zwölf Proben zur Analyse entnommen: Zwei archäologische Proben, eine aus dem Putz des Beckengebäudes und die

andere aus dem Mörtel der Nordwand der Stätte MRB-05-001, und um die Herkunft der Rohstoffe für Mörtel und Putz zu ermitteln, wurden die anderen zehn Proben aus Playa-Sedimenten entnommen. Für die IR-Analyse wurde das FTIR 8400S von Shimadzu (Japan) verwendet. Es wurden KBr-Pellets vorbereitet, um Spektren der Proben im Spektralbereich zwischen 4000 und 400 cm⁻¹ mit einer Auflösung von 4 cm⁻¹ zu erhalten. Für die EDRFA-Analyse wurden die Proben mit Mörser und Stößel zu einem Pulver zermahlen und dann 1 Gramm in eine 2 cm² große runde Scheibe gepresst. Die Röntgenisotopenquelle wurde zur Messung der Proben verwendet, wobei ¹⁰⁹Cd mit einer regulären Energie von 22,6 Kev verwendet wurde. Der Si(Li)-Detektor, das CANBERRA-VerstärkermodeLL 2020, wurde mit einer Hochspannungsversorgung von 600 V eingerichtet. Die Ergebnisse zeigen einige chemische Elemente und Komponenten, die auf eine Ähnlichkeit zwischen den beiden archäologischen Proben (Mörtelprobe von der Nordwand und Beckenputzprobe an der Stätte MRB-05-001) und Playa-Proben aus drei Bereichen (MRB, MOH und KOG1) hinweisen.