The Crucifix Chapel of Aci Sant'Antonio: Newly discovered frescoes

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In this paper we present the discovery of a series of frescoes for the first time, revealed in 2012 during a restoration carried out in the Crucifix chapel in the Mother Church in the town of Aci Sant'Antonio, Sicily. The mural paintings were preserved in each of the corners of the square chapel, behind an early 20th century counter wall. In this paper, we also show the application of multispectral imaging (MSI), portable XRF spectroscopy (pXRF) and Fiber Optics Reflectance Spectroscopy (FORS) for the identification of pigments on this interesting case of mural paintings. Documentation from the 20th century remodeling is available, and when taken into account along with this case study, represents an interesting case of "terminus ante quem" (TAQ) chronology since we are aware of the date when the last retouching to the square chapel walls could have been applied.

The Mother Church of Aci Sant'Antonio was originally built in 1566, and dedicated to Sant'Antonio. In 1693 it was rebuilt in the then current baroque style after a destructive earthquake occurred. Its internal layout forms a Latin cross with three naves, a transept and side chapels. Inside the church, several kinds of liturgical artworks are conserved, such as the wooden choir, and the frescoes by Pietro Paolo Vasta situated along the walls and the vault of the apse. Pietro Paolo Vasta (Acireale, 1697-1760) is considered one of the leading figures of Sicilian art. In 1734 the painter opened a workshop in Acireale where he received other artists as apprentices, such as Michele Vecchio, Alessandro Vasta (his son), and Giuseppe Grasso Naso. The Crucifix Chapel is the closest one to the apse, along the left nave, figures 1 and 2. It has an octagonal floor plan, which was realized within the original square-shaped one. During the maintenance works on the ceiling, carried out between 2012 and 2013, the original shape and features of the chapel were revealed. The current octagonal arrangement is dated to the beginning of the 20th century, and the new walls are joined to the preexisting ones with tie-hooks in only a few places. The discovery of the 18th century frescoes made it necessary to pause the current restoration work and reflect on the best way to represent the space. The choice was made to maintain the octagonal shape of the chapel, while making the frescoes in the corner niches visible by way of large windows.

The original cycle of paintings was spread across the four walls of the square room. The paintings represent classic themes of the last days of earthly Christ: Last Supper; Jesus meets the Virgin, which, in the Sicilian folk tradition represents the last moment before Christ ascends to Heaven (there are no traces of this episode in the Holy Scriptures);

Fig. 1 - Crucifix Chapel, Mother Church, Aci Sant'Antonio. Split panorama of the chapel after the renovation. The murals were found in 2012 during renovation works, and the windows at each of the four corners allow the 18th century frescoes decorating the original chapel to be seen.

Agony in the garden; Kiss of Judas; Flagellation; Jesus at the column; Flagellation in Via Crucis; Jesus fallen down under the Cross; Crucifixion.

This cycle of frescoes is attributed to the painter Giuseppe Grasso Naso, pupil of Pietro Paolo Vasta, as the execution style corresponds to other mural paintings completed by the artist. Moreover, Don Vittorio Rocca, the priest of Aci Sant'Antonio, has found documentation. The account book of the Mother Church for the period between 1768 and 1792, figure 3, declares a payment to Grasso Naso, and thus validating the attribution of the artwork to the Sicilian painter and dating the paintings to the 18th century. The painter would have worked in the chapel just a few years after Vasta had completed the frescoes in the presbytery.

The first few lines of text on page 102 are a record of the payments made to the artists working on the decorations of the chapel from the end of August, 1773.

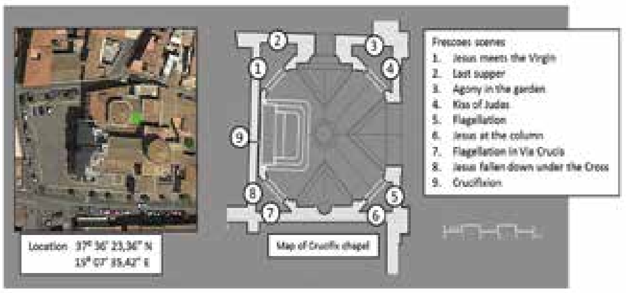

Fig. 2 - Crucifix chapel, Mother Church, Aci Sant'Antonio. Drawing of the floor plan with location of the frescoes and description of the scenes represented.

Fig. 3 - Photograph of the archive showing financial transactions of the Parish from the month of August, 1773 to the painter Giuseppe Grasso Naso.

"In primis onze 10:4 tarì pagati a Don Giuseppe Grasso pittore e al maestro Cristofalo Grasso come per mandato spedito a 23 agosto 6 ind. 1773."
10 *onze* and 4 *tarì* payed to Don Giuseppe Grasso painter and to master Cristofalo Grasso as per mandate sent on 23rd August 6th ind. 1773.
"Onze 6 al sig. Don Alessandro Vasta pittore per mandato spedito a 31 agosto 6 ind. 1773."
6 *onze* to Don Alessandro Vasta painter as per mandate sent on 31st August 6th ind. 1773.
"Onze 2: tarì 9 al signor Mariano Leotta doratore e per mandato spedito 31 agosto 6 ind. 1773."
2 *onze* and 9 *tarì* to Mariano Leotta guilder as per mandate sent on 31st August 6th ind. 1773.
"Onze 3 e 4 tarì a maestro Nunzio Grasso come per mandato spedito 31 agosto 6 ind. 1773."
3 *onze* and 4 *tarì* to master Nunzio Grasso as per mandate sent on 31st August 6th ind. 1773.

The onza and the tarì were the coins circulating in Sicily during the 18th and 19th century, until the unification of Italy in 1860. Each onza (4.4 g of gold) corresponded to 30 tarì. The quoted name, "Giuseppe Grasso painter" refers to Giuseppe Grasso Naso (Acireale, 1726-1791), a pupil of Pietro Paolo Vasta, not Giuseppe Grasso (Acireale, 1759-1800) who was known as Giamingo.
Overall, the paintings appear to be in good condition; however, those on the North wall (same side as the altarpiece) show signs of deterioration. Here, a substantial difference in the state of conservation occurs due to the presence of moisture, which has caused the plaster layer to crack, resulting in localized detachments. The chapel was incorporated within the internal area of the church, making it protected from the weather to a height of about 3.8 meters. However, the wall where the altarpiece is positioned is external with respect to the church, making it more vulnerable in general to water damage. Therefore it remains that the upper part of the painted areas is drier and better preserved while the decorative frames seem to have been refashioned several times over the centuries. The presence of moisture must have been more evident before the 19th century and before the construction of later additions. The construction of the octagonal chapel resulted in drops of lime ($CaCO_3 \, nH_2O$) being splashed onto the adjacent paintings. Additionally, in several points it is possible to observe abrasions and holes from incidental damages caused by the equipment necessary to build the walls of the new chapel.
The main objectives of the scientific investigations presented in this paper, multispectral imaging, pXRF, and FORS were to identify pigments and localize areas of later retouchings on the wall paintings, thus obtaining very pertinent information which would be used to guide the cleaning intervention. To the best knowledge of the authors there is only one other published work on frescoes linked to the school of Paolo Vasta [1].

INSTRUMENTATION

Multispectral Imaging
Multispectral imaging (MSI) [2, 3] is used for the non-destructive identification of pigments. This study illustrates MSI images in 3 spectral bands: Ultraviolet, UV (360-400 nm); Visible, VIS (400-780 nm) and Infrared, IR (780-1100 nm). The acronyms for the MSI methods presented in this paper highlight first the spectral band followed by R (Reflected), F (Fluorescence), FC (False Color). So the 5 imaging methods are called VIS (Visible), IR (Infrared), UVF (UV Fluorescence), UVR (UV Reflected) and IRFC (Infrared False Color). It is mandatory to point out that, due to the nature of the painted surface, these optical methods are problematic and the user may be subjected to make interpretations and draw conclusions that remain uncertain. Therefore, to identify pigments with an acceptable degree of certainty, at least one other material specific technique must be employed, such as pXRF and FORS used in this study.
The MSI images presented in this paper were acquired with a Nikon D800 DSLR (36 MP, CMOS sensor) digital camera modified for "full spectrum", ultraviolet-visible-infrared photography (between about 360 and 1100 nm), figure 4. The CMOS sensor responds both to the near infrared and near ultraviolet ranges of the spectrum and the manufacturer installs an IR cut-off filter in front of the sensor to reduce infrared transmission. There are companies that remove this filter in commercial cameras, which are then said to be "full spectrum". The Nikon D800 camera was tethered to a computer to allow sharp focusing in non-visible modes (IR and UV) using live view mode. The filters used for the MSI were: a) For Ultraviolet Reflected (UVR) photography, the B+W 403 filter together with the X-NiteCC1. The B+W 403 allows just the UV and IR light to pass, and the X-NiteCC1 is necessary to stop the IR produced from the UV lamp; b) For Visible (VIS) photography, just the X-NiteCC1 filter is sufficient; c) For UV Fluorescence (UVF) photography, the B+W 420 must be mounted to stop the reflected UV, and the X-NiteCC1 is also necessary to exclude any infrared from the UV lamp; d) For Infrared (IR) just the Heliopan RG1000 is used. A Nikon Nikkor 200 mm f/4 AI manual focus lens was used for all the

MSI photos produced using the panoramic method [2]. Two 1000 W halogen lamps were used for VIS and IR photography; for UV photography, one high-Flux 365nm LED lamp was sufficient.

Fig. 4 - The panoramic multispectral imaging system used to document the mural paintings in the Crucifix Chapel.

X-ray Fluorescence Spectroscopy

The multispectral imaging was complemented by a qualitative elemental analysis carried out using portable x-ray fluorescence spectroscopy (pXRF), figure 5. The instrument used was a handheld Bruker AXS Tracer III-SD® (Kennewick, WA USA), equipped with a Rh anode for the production of x-rays, operating at 40keV maximum voltage, and capable of selecting a tube current between 2-25 μA. Spectra were collected by means of a Si-SDD detector with a resolution of 145 eV, FWHM at Mn (5.9 keV). Detector and source are orientated in 45° geometry, and the spot size is of elliptical shape approximately three by four millimeters (9.4 mm2). All measurements were performed in air, with a voltage of 40 kV, a current of 11.2 μA, and an acquisition time of 30 seconds. These settings allowed the detection of elements of atomic number 13 (Al) or higher, however the detector is most efficient in identifying elements above atomic number 20 (Ca). The settings also provided a sufficient raw count rate (range 50,000-110,000, avg. 90,000) to acquire representative spectra without saturating the detector. Measurements were taken at an assortment of points selected to include each of the colors used in the palette in one or two different areas on each of the paintings. The instrument was operated in the field using a rechargeable Li-ion battery and a laptop computer for control and data storage. A total of 28 spots were analyzed, 13 on the painting the *Kiss of Judas* and 15 on the painting the *Flagellation*. Spectra were subsequently processed and visualized using Bruker ARTAX software. The approach taken with the pXRF analysis was to acquire qualitative elemental readings on the materials present in the pigments used in the wall paintings. This was to be a quick point-based assessment that would serve to complement the more "global" analysis carried out with multispectral imaging.

Fig. 5 - Acquisition of pXRF spectra on the Flagellation mural painting in the Crucifix Chapel.

Fiber Optics Reflectance Spectroscopy

It was used a portable and miniaturized Fiber Optics Reflectance Spectroscopy (FORS) system whose features are well described elsewhere [4]. Spectra have been acquired with the following parameters: integration time: 5 sec; scans to average: 4; boxcar width: 5. The Ocean Optics integrating sphere ISP-R has been used to acquire the spectra on the same areas as for the pXRF analysis on the Kiss of Judas mural painting. The FORS spectra were compared with those in a database of pigments laid with the fresco technique [4]. Unfortunately, the reference FORS spectra of emerald green and chrome yellow - pigments identified by pXRF - are not available and the FORS identification could not be made.

RESULTS AND DISCUSSION

Two of the four murals were examined, the *Kiss of Judas* and the *Flagellation*. Table 1 shows the list of areas examined with pXRF. The FORS system was applied on the same areas but only on the Kiss of Judas. The presence of some paint losses on the figures in both the two mural paintings allowed for the direct pXRF analysis of the preparation layer which provided the same conclusions about the support. For example, area 8 in the *Kiss of Judas*, was shown to be rich in calcium and sulfur. The calcium content is expected and compatible with the fresco technique; however the elevated presence of sulfur is likely due to on-going degradation processes, both organic and inorganic, which lead to the formation of sulfates in the superficial patina [5].

THE KISS OF JUDAS

Thirteen areas on this mural were selected for pXRF analysis, figure 6.

Greens. In areas 1 and 2, the paint has been applied "a secco" as evidenced by the numerous losses. The XRF spectra indicate Cu and As as the two major elemental components of the pigment. There are two arsenic-based green pigments: Scheele's green and Emerald green [6]. The first is ruled out because its color ranges from pale yellow-green to deep green and it is known to darken over time. Scheele's

Fig. 6 - Areas analyzed by pXRF and FORS on The kiss of Judas mural painting.

green, a copper arsenite of varying composition, was the first synthetic green copper arsenic pigment (1778). Emerald green, a copper acetoarsenite, is likely to be the pigment used in this painting. It was introduced between 1800 and 1814, and it is no longer available as an artists' pigment because of its toxicity; it has a brilliant blue-green hue, which matches the one observed in this mural painting.

The darker shade of green analyzed in area 6 is green earth as suggested by the iron content. The corresponding FORS spectra are flat and do not have characterizing features useful for its identification. The brighter greens, represented in areas 7 and 9, contain a considerable proportion of lead, and therefore they should be a mix of green earth and lead white, added to obtain the lighter hue. Lead white is a problematic pigment for frescoes since it is known to darken [7], however this problem occurs mostly on outdoor murals.

Yellows. On the bottom border of the mural, area 3 is shown to have been retouched with 19th century chrome yellow [8]. This is a relatively inexpensive yellow pigment with high covering power, which was in use (along with the other chrome pigments) by 1816 but on a limited basis.

Scene	Area #	Color	Major Elements	Minor Elements	Pigments
Kiss of Judas	1	light blue	Cu, As, Ca, S	K, Fe, Sr	emerald green
	2	light blue	Cu, As, Ca, S	K, Fe, Sr	emerald green
	3	yellow	Cr, Fe, Pb, S	Ca, Sr, K	chrome yellow
	4	brown	Fe, Pb, Ca, S	Si, K, Sr	earth based
	5	white	Ca, S, Pb	Fe, Sr	calcite / gypsum / lead white
	6	dark green	Fe, Pb, Ca, S	Mn, Si, K, Sr	green earth / umber
	7	green	Pb,	Ca, Fe, S, Sr, Si	green earth / lead white
	8	white	Ca, S, Sr	Pb, Fe,	gypsum
	9	light green	Pb, Ca,	Mn, Fe, Si, K, Sr	green earth / umber
	10	red	Hg, Pb, S	Fe, Ca, Sr	vermilion / lead white / ochre
	11	red	Fe, Ca,	Hg, Pb, S, Sr	red ochre / vermilion
	12	blue	Pb,	S, Ca, Fe,	lead white / ?
	13	blue	Pb,	As, S, Ca, Fe,	lead white / ?
Painting	**Area #**	**Color**	**Major Elements**	**Minor Elements**	**Pigments**
The lagellation	1	red	Fe	Ca, Hg, Pb, S	red ochre / vermilion
	2	red	Fe	Ca, Hg, Pb, S	red ochre / vermilion
	3	tan	Pb		lead white
	4	light blue	Cu, As, Ca, S	K, Fe, Sr	emerald green
	5	tan/white	Pb		lead white
	6	brown	Pb,	Ca, Fe	lead white with earth
	7	brown	Pb,	Ca, Fe	lead white with earth
	8	white	Ca, S, Pb	Sr	calcite / gypsum / lead white
	9	tan/white	Pb		lead white
	10	tan/white	Pb		lead white
	11	tan/white	Pb		lead white
	13	green	Fe	Ca, Pb, K	green earth / lead white
	14	light blue	Cu, As, Ca, S	K, Fe, Sr	emerald green
	15	green	Pb, Fe, Ca,	Cr, Sr	green earth / veridian
	16	green	Fe, Ca, Pb	Cr, Sr, K	green earth / veridian

Table 1 - Summary of pXRF data for the two mural paintings analyzed.

Because the pigment tends to oxidize and darken on exposure to air over time, and it contains lead, a toxic, heavy metal, it has been largely replaced by cadmium yellow in today's market. This chrome yellow paint appears to have been applied over an older and original yellow layer of paint, which analyzed in area 4, confirmed a more typical yellow earth (yellow ochre or umber). The FORS spectrum shows the characteristic S- shape and the presence of two broad absorption bands near 660 nm and 930 nm, which are attributed to goethite, confirming the identification of yellow ochre, figure 7.

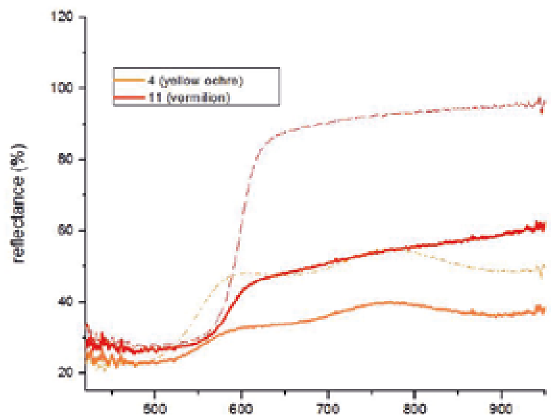

Fig. 7 - FORS spectra of areas 4 and 11 on the Kiss of Judas mural painting. Dotted lines are the reference spectra of corresponding pigments applied on fresco.

Whites. A thin layer of lead white, analyzed in area 5, has been used to whitewash the original caption. However, most of it has disappeared and the original caption is almost entirely readable.
Reds. As shown by the IR image, figure 8, a red pigment used for Jesus' vest strongly reflects IR, which rules out the use of red earth pigment. Complementary to this information, the pXRF spectrum shows that the pigment is rich in mercury, (areas 10 and 11) confirming the use of vermilion. This identification is supported also by the FORS spectrum of area 10, figure 7.
Blue. The blue pigment for Jesus' mantle absorbs the infrared and turns a reddish/purple color in the IRFC, figure 8. Two areas (12 and 13) were selected on the mantle for pXRF analysis and lead was the only element shown to have a significant contribution to the spectra. The FORS spectra are flat and do not help in the identification. The lead content observed in the pXRF spectrum likely belongs to lead white used to brighten the blue pigment. Since the spectrum presents no other major peaks, it stands to reason that the blue pigments based on metal elements (azurite (Cu), Prussian blue (Fe), Cobalt blue and smalt (Co)) are not present in the areas studied. In this case, we may rule out some blue pigments, however, a blue pigment identification cannot be positively confirmed using only the techniques employed in this preliminary study, since also the FORS spectrum had not characterizing features.

Flagellation
Sixteen areas on the painting *The Flagellation* were selected for pXRF analysis, figure 9. The multispectral imaging is shown in figure 10.

Reds. The pXRF spectra of areas 1 and 2 show a large content of mercury, which together with the high infrared reflectance, confirm the pigment vermilion.

Fig. 8 - The kiss of Judas mural painting. Visible (left) Infrared (middle) and infrared false color (right) images. The red pigment of Jesus' vest strongly reflects infrared, and appears yellow in the IRFC, suggesting vermilion. A cleaning test, visible in the middle of the scene (see dashed line), was administered in order to evaluate both the texture and the state of conservation of the frescoes.

Whites. Lead white was used for the pavement, confirmed in the analysis of areas 3, 5, 6, and 7. Lead white was also mixed with ochre on the drape, evidenced in the spectra from areas 9, 10, and 11, which show an elemental content composed mainly of Fe and Pb.

Fig. 9 - Areas analyzed by pXRF on the Flagellation mural painting.

Fig. 10 - The Flagellation mural painting. Visible (left) and details: visible (top left), infrared (top right), infrared false color (bottom left) and UV fluorescence (bottom right).

Greens. The same arsenic-based Emerald green is found in the bluish-green band on the border, analyzed in areas 4 and 14. Green earth is found on the lower green decoration, area 13, and on the pedestal, areas 15 and 16, also with some viridian, as indicated by the chrome content. Pannetier, a color maker in Paris began to make chromium green in 1838 and viridian soon replaced the toxic Emerald Green. An interesting note was that in all of the spectra, except those of the light blue areas, there was an abundance of lead, indicating the extensive use of lead white throughout the paintings. The light green areas showed a high concentration of both copper and arsenic in the ratio of 1:1, in accordance with the composition of the pigment emerald green. We can tell by the close observation of Jesus' right hand, that the underdrawing was probably performed by tracing the outline of the figures using a dark brown pigment and thin paintbrush, figure 11.

The ultraviolet radiation excites the organic molecules present on the surface of the artwork, producing a pale fluorescence and revealing the presence or the alteration of organic components present on the surface. In this way, it is possible to locate and assess the presence of a biological colonization (some bacteria have their own peculiar fluorescence), of retouches made by the artists themselves, of particular organic colorants, or previous restoration compounds.

In the fresco technique, the principal paint binder used to fix the pigments to the substrate is slaked lime. Once the fresco is dry, the artist is able to make final retouches and details using the tempera technique (egg yolk and/or milk). While calcite doesn't emit fluorescence under UV light, the paint bound by tempera does. In figure 11 and 12, tempera retouchings on the dresses and on details of the faces, the floor tiles and hands are indicated by their UV fluorescence.

CONCLUSIONS

The mural paintings are made "a fresco" in wet plaster with "a secco" (dry) finishing touches, as was common in the 18th century. This process allowed the artist better management of the retouching and working times. However, it also has

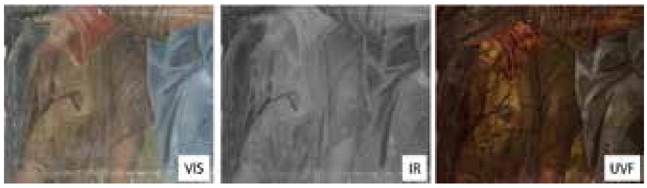

Fig. 11 - Flagellation, area where a cleaning test was performed, framed by the dotted white line. UV fluorescence is evident on the dress highlights.

Fig. 12 - The Flagellation. A secco retouches exhibit strong UV fluorescence.

the disadvantage of the end result being more delicate than the traditional "buonfresco" technique. It was also shown that the mural paintings have been carried out using the same palette of typical earth based fresco pigments, which has been documented in contemporary frescoes from the same school of artists operating in Sicily [1]. Vermilion was found on both of the two murals. This is a relatively expensive pigment for murals where red ochre would instead be more commonly used. Viridian is the only modern pigment found on the figures. More extensive interventions with 19th century pigments (emerald green and chrome yellow) were found only on the bottom frame which is clearly subject to more aggressive degradation caused by capillary rise of water. The investigation allowed to identify some of the restorations performed before the damaged walls of the chapel were eventually enclosed during the 20th century remodeling which obliterated the memory of the frescoes to the community until their recent rediscovery.

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AUTHOR CONTRIBUTIONS

Aci Sant'Antonio is the hometown and residence of Antonino Cosentino, who works as a cultural heritage scientist providing consulting and training as a private service. He offered to volunteer his time and equipment in order to provide scientific support to the ongoing restoration project, and the architect in charge of the restoration of the chapel, Raffaello di Mauro, accepted. Dr. Cosentino also was able to involve Camilla Perondi, a student in Technology for Cultural Heritage at University of Bologna; and Samantha Stout, a PhD student in Materials Science and Engineering at the University of California, San Diego.

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Abstract

Questo lavoro presenta per la prima volta la scoperta di una serie di affreschi effettuata nel 2012 durante il restauro della cappella del Crocifisso nella chiesa madre di Aci Sant'Antonio, Sicilia. Le pitture murali si sono conservate in ognuno degli angoli della cappella quadrata dietro le contropareti aggiunte all'inizio del XX secolo. In questo articolo si mostra anche l'applicazione combinata dell'imaging multispettrale (MSI), della spettroscopia di fluorescenza X portatile (pXRF) e della FORS per l'identificazione dei pigmenti su queste pitture murali da poco scoperte. Dopo una ricerca d'archivio, e' stata ritrovata la documentazione degli interventi che hanno portato alla copertura degli affreschi. Dal momento che siamo al corrente dell'anno in cui gli ultimi interventi sugli affreschi possono essere stati eseguiti, questi murali rappresentano un interessante caso di cronologia "terminus ante quem" (TAQ), in particolare per quel che riguarda l'uso dei pigmenti.

Keywords

bronze objects; corrosion; SEM; XRF; XRD; treatment; conservation

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