Technology and Provenance of Stone, Plasters and Pigments

General

025   A Study of Painting Layer Used in the Anthropoidal Wooden Coffins from the Late Period (Giza Storage)

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During the excavation of Kut Abu Zied in El-Mansouria area, Giza (1988-89), a number of anthropoid wooden coffins dating back to the late period were discovered and later on transferred to the Giza Archaeological stores. A fine plaster covered all the details of these wooden coffins. The decorations of this plaster layer were composed of a collar, seweret, eye panel and several columns of text and painted with different color.

Four anthropoid wooden coffins from the group of coffins that had been discovered were chosen for this study, which were registered under no 480, 482, 483, 485 respectively, in the archaeological stores of Giza. The coffins are closed and still contain the mummies. They were badly weakened and covered with dirt, they have many cracks in the headdress area, the sides and in the foot parts. Plaster layers are separating from the substrate along the foot end and on the side of the face. Coffin no 482 was broken into several pieces and has many cracks in all the body, and the wood is very fragile.

Samples of plaster and pigment from the four coffins were analyzed in this study by using light and polarizing light microscopy, X-ray diffraction analysis, scanning electron microscope with the energy dispersive X-ray spectrometer, and infra red analysis.

It was found that coffins no 482 and no 483 consist of small wooden pieces, while coffins no 480 and no 485 consist of large wooden pieces; all coffins were made of local Sycamore. Plaster layers were made of calcite and hematite. In coffin no 480 hematite was used to obtain the rosy color. Blue pigment used in the coffins is Egyptian blue. Tin, zinc and lead detected by EDS study in coffins no 480 and no 485 could have been obtained from metal alloys which were used in the preparation of Egyptian blue. The dark blue phase in coffin no 483 gave rise to the suggestion that the pigment was prepared in the temperature between 850-950ºC, with a high percentage of copper. The light blue phase in coffin no 485 gave rise to the suggestion that the pigment was prepared with a high percentage of quartz.

Atacamite detected as a green pigment in coffin no 480 indicates that it was prepared for use as a pigment by mixing a copper compound with sodium chloride in a humid atmosphere prior to application. Results of the studied green pigment in coffin no 485 indicate that it was green frit (copper wollastonite), which contains a low amount of goethite. Polarizing microscopy studies detected that goethite was present in some parts separated from the green frit, which means that it may have been used for preparing the surface to reach a deep color. Red pigment in all coffins is hematite, white pigment is calcite and black pigment is carbon. Infra red analysis of the used media indicates that animal glue was used as medium in the four coffins.
A New Source of Obsidian on the Aegean Island of Yali

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The sources of workable obsidian in the Aegean, which have been reported and studied so far are located on the Cycladic islands of Melos (at two sites), Antiparos and on Yali in Dodecanese, although more occurrences of non-workable obsidian are geologically known in a number of outcrops at western Thrace, on the islands of Thera, Kos, Nisyros etc. Here for the first time we report a second source of workable obsidian, recently discovered on the small island of Yali.

Pyroclastic material of various types (pumice, pumice stone, volcanic ashes etc) predominate the SW part of the island, while in the NE part mainly leucocratic rhyolites occur, deposited during an upper Pleistocene submarine ejection. The already known source of Yali obsidian appears as angular small flow folds, alternating with the rhyolites, in several sites of the NE part of the island. This kind of obsidian, although available in large pieces, bears characteristic gas vesicles or microcrystalline aggregates spaced every few millimeters throughout the mass, thus prohibiting construction of small objects (blades, arrowheads etc). For this reason dispersion of prehistoric obsidian objects constructed from the above raw material was rather limited, in comparison to objects made of the supreme quality Melian obsidian.

The new source provides rounded or irregular-in-shape pieces of black or dark-gray obsidian, free of inclusions. Such pieces are rather usually apparent in the pumice layers of the SW part of the island. Their dimensions vary from 2 to about 15cm although thump-sized pieces are not uncommon, according to our field observations.

Laboratory studies showed that the recently discovered obsidian is in quality fairly comparable but chemically distinguishable to the Melian obsidian, while at the same time workable by prehistoric man.

Current analytical work is now focused on the geochemical characterization of the new Yali obsidian source, as well as on investigation of its usage in the Neolithic settlement of Yali, studied in the past.

Atlas of Prehistoric (Non-metallic) Raw Materials in Hungary

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With the support of OTKA Project T-025086, a four year interdisciplinary collaboration project was performed between 1997-2001 on the research and mapping of non-metallic prehistoric raw materials in Hungary. The original geographical scope of the project aimed at surveying the territory of the Carpathian Basin as a relatively closed geographical-historical unit in prehistorical times. The level of information available, however, is fairly uneven for large part of the area therefore we cannot claim to be representative over all the possible contact region of the former inhabitants of this territory.

Our method was collecting available pieces of petroarchaeological/archaeometrical information from Hungary and compare them with mapping geological data. Non-metallic raw materials were grouped in three large categories: stone tools, pottery, others. Existing/established type groups (mainly macroscopic type groups) were selected, presented on series of maps. Possible geological sources were collected within Hungary (when sources exist here) and in the wider environment (Carpathian
Basin, Central Europe etc. when known). Extraction sites and "workshops" were specifically selected and level of scientific information (macroscopic analysis, instrumental analytical techniques when existing) recorded. The level of knowledge on certain categories, especially chipped stone raw materials is fairly advanced due to many years of research and systematical comparative collections. In some other cases, like polished stone tool raw materials, the evidences are currently gathered by the help of international projects (IGCP-442, MÖB-DAAD). In a lot of instances, however, like provenancing sandstones or pottery, we are just in the phase of raising the questions.

This type of information is constantly growing. Categories tend to move by the advance of research, as we can determine the origin of pieces better (or worse…) by the advance of analytical studies day by day. Therefore we decided to present results on a series of maps available through Internet for interactive handling. The (preliminary) test pages are available already at the Internet (http://reg2000.ace.hu/atlas/) while the final version will be installed by the time of the 33rd ISA meeting in April at http://www.ace.hu/atlas.

028 Preliminary Results on Canarian Obsidians from Gran Canaria Island

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Human presence in Canary Islands can be traced back to the middle of the 1st Millennium BC. The original population comes from Northern Africa and it belongs to the paleo-Berber group. The Islands were afterwards re-discovered by Europeans at the end of the Middle Ages, and they were gradually incorporated to the Castilian Kingdom along the 15th century. During this long ‘prehistoric’ period before the European influence, each island of this archipelago developed a particular culture with his own characteristics. In the case of Gran Canaria Island, the society exhibits a hierarchical complex structure and the economy is based on a re-distribution network of goods, among which obsidian, which was exploited at least since the New Era, seems to have played an important role.

Even if different obsidian sources are known within the island, most of them are of a small size and the only one that shows clear evidence of an organized exploitation, with numerous mining galleries, is the one at Hogarzales mountain. In a current research project on obsidian sources exploitation and artefact production in Canary Islands, a first archaeometric phase has been devoted to the characterisation of Hogarzales obsidian.

Several samples have been taken from different galleries and from several debris dumps, as well as from archaeological objects recovered at different sites all around the island. All samples have been analysed by neutron activation analysis (NAA), inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). In that way, this first phase has enabled the characterization of one of the most important obsidian sources exploited in antiquity, and also the inter-comparison of the techniques employed.
Byzantine and Seljuk periods are two important overlapping cultures in Anatolia. It is important to understand whether these two cultures had strong exchanges and whether one culture became the continuation of the other.

In this study, plaster technology belonging to those two cultures have been investigated in the monuments related to those periods in the same and in different localities. By this way, it is aimed to find out the common features and the differences of these two cultures. Since these plasters have survived on the standing monuments through centuries, their characteristics will also help to the description of durable plasters.

Analyses were made to determine physical and mechanical properties of plaster layers located on the interior and exterior wall surfaces, raw materials composition of the layers as binder and aggregates, whether additives have been put to develop pozzolanic properties and/or to affect carbonation reactions of binder lime. For the painted plasters, the pigments and the painting techniques were also examined.

The physical and mechanical properties of the plasters were studied by the measurements of bulk density and total porosity using RILEM standard test methods, and ultrasonic velocity measurements. Petrographic properties and mineralogical composition were determined through thin section analyses by an optical microscope and by SEM coupled with EDX and XRD analyses. Pigments were also analysed by chemical spot tests and FTIR. Particle size distribution of aggregates was done by sieve analyses. Finest aggregate fraction (< 125µ) was examined for its pozzolanic activity by change in conductivity of saturated Ca(OH)₂ solution. The properties of the binder were more closely examined by the help of white lumps in the plasters not mixed with the aggregates.

The bulk density of rough plaster layers were in the range of 1.30-1.80g/cm³ and the total porosity in the range of 22 to 49 percent by volume. Ultrasonic velocity measurements varied in the range of 1200 to 2100m/s. The finest aggregates had considerable pozzolanic activity which may have contributed to mechanical strength of the plasters. The binder lime was pure micritic calcite with a few percent of clay minerals and possibly some organic additives. The results were further discussed in terms of abundant red pigments and their mineral sources, raw material characteristics of binder, aggregates, additives and the durability characteristics of plasters. The results were also interpreted for the preparation of new repair plasters.

The aim of this work has been mainly to set up a new methodology useful to recognise the kind of limestone utilised in the preparation of the lime used as binder in ancient mortars.
On the occasion of the study of the static conditions of the bridge known as the “Ponte di Augusto” erected over the river Nera we carried out a research on the mortars used for the building. The Ponte di Augusto, built 27 BC during the works of enlargement of the consular way, is one of the widest ever erected by the Romans and is sited close to Narni, in Umbria not far from the Latium border. Narni was founded by the Sabin people and then turned in a Roman colony (Narnia) which had a strong military importance because of its strategic position on the "Flaminia way". At present only one arch is standing which should not be the widest. Its chord is 20m long and its height at the intrados is 27m. The arches, the piers and the abutments were made by a framework of well cut travertine ashlars filled with a mortar that shows a really strong cohesion with mechanical characteristics similar to that of the modern concrete. The Romans realised a high-quality mortar of relative low porosity (~ 30%) and strong mechanical characteristics. These good characteristics appear mainly to be ascribed to the use of a binder of high hydraulicity.

The comparison between chemical and mineralogical analyses performed on binder and lumps evidenced that the high hydraulicity was not obtained by the addition of particular additives like pozzolana. Hence the research was directed towards the individuation of the possible local limestone whose chemical composition best fitted the chemical data of the mortar’s binder. Because of the presence of many limestones of different age that show a chemical composition similar to that of the binder, we thought about a micropaleontological approach. Micropaleontological analyses has been performed in order to detect both the presence of relics of calcareous and/or siliceous fossils inside the binder resisting to burning and for the determination of the age of the original limestone. This kind of analysis revealed to be promising and an experimental study was set that consisted in the realisation of mortars from the calcination of different types of limestone coming from the outskirts of Narni. A micropaleontological study has been subsequently performed on the binder of these mortars.

031 Characterization of White Lead Pigments by Voltammetry of Immobilized Microparticles

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The voltammetry of immobilized microparticles (VIM) was used for the characterization of white pigments, based on lead compounds, because it is a non-destructive, inexpensive and easy to handle technique.

The possibilities of this electrochemical analytical technique were already shown in a previous paper. This electroanalytical technique is based on a mechanical transfer of traces of a solid sample onto the surface of a solid electrode and the subsequent recording of a current-voltage curve. However the transfer of material can be done just by gently rubbing the surface of the end of the electrode on the material surface or transferring a very small quantity (about one nanogram) to the electrode, so without any damage on the sample.

The electrochemical characteristics of lead carbonate (PbCO₃), basic carbonate (2PbCO₃·Pb(OH)₂) and sulphate (PbSO₄), and lead carbonate-sulphate mixtures were studied and this identification was applied to the analysis of several commercial white pigments.

The results showed that, in all cases, it was possible to differentiate the main compounds that were used to produce the white colour. The electrochemical parameters could be also used to study pigment alterations and to identify the introduction of modern pigments. This study could be also extended to the research of lead-glaze alterations, which generate lead carbonate or sulphate.
Magnetic Properties of Obsidian and Provenance Studies in the Neolithic of Western Mediterranean

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During the Neolithic, obsidian was widely used in islands of the Western Mediterranean basin and in its bordering areas. Previous studies based on geochemistry and/or fission-track dating demonstrated that in these regions the raw material came from only four source-islands: Lipari, Palmarola, Pantellaria and Sardinia.

Revisiting the potentialities of structural characterization in sourcing studies, we showed that Mössbauer spectroscopy and possibly ESR (Scorzelli et al. 2001) could offer viable alternatives. We show here that variations in the magnetic properties (MP) of obsidian show also a great potential in provenance determination and thermal history of stone tools. In particular, MP offer a fast and economic approach at least for the considered area, since in recent years the improvement of magnetization measurement techniques, as SQUID, made possible the study of samples with very small magnetic signals (down to $10^{-7}$ EMU).

The samples studied were either artefacts of independently determined provenance or well documented geological samples. The magnetization signal of this material originates predominantly from the paramagnetic glassy matrix while the saturation remanent magnetization $\sigma_r$ and the coercive force $H_c$ are due to ferrimagnetic grains of different sizes. The magnetic hysteresis properties of the samples were obtained applying a magnetic field (±1.5T) at 300K, with a Quantum Design SQUID magnetometer. In order to obtain the saturation magnetization $\sigma_s$ of the samples a linear extrapolation of the paramagnetic contribution to $\sigma$ was made using $H \to 0$. In a plot of the relative saturation magnetization $\sigma_r/\sigma_s$ vs relative coercive force $H_c/H_{cr}$, obsidian specimens from different source-islands are located, with only few exceptions, in discrete areas. This property might be exploited as an alternative approach to provenance studies.

Reference

Obsidian Trade Connections at The Postclassic Maya Site of Laguna De On, Belize

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Obsidian tools were an important component of the utilitarian economy of the Postclassic Maya site of Laguna de On, Belize, where they outnumber tools made of local chert and chalcedony. Sourcing of obsidian blades from Laguna de On was done by dispersive X-ray fluorescence spectrometry. Trace element content of the Laguna de On obsidian blades was compared to that of obsidian from known geological sources. The trace elemental analyses for all samples was conducted under the same conditions. Trace elements used were rubidium (Rb), strontium (Sr), yttrium (Y), and zirconium (Zr). The obsidian samples were bombarded with X-rays from a tin target acted upon by radioactive Americium-241. The trace elements contained in the obsidian sample were among the X-rays it emitted, where the concentration of the element was measured by the intensity of its X-ray and the type of element by its spectral position.
Data presented here indicate that obsidian blades from the Ixtepeque source, 95%, far outnumber obsidian blades from other Highland Guatemala sources during the Postclassic Period. These data agree with the literature that during the Postclassic in Mesoamerica obsidian used in the Maya Lowlands came primarily from the Maya Highlands with little importation of Central Mexican sources, a phenomenon that occurred in earlier periods.

034 Painted Astragaloi (Knuckle Bones) from the Cave of the Nymphs on Mount Helikon: New Evidence on Ancient Greek Polychromy

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In antiquity, astragaloi (knucklebones) from sheep or goat, were used in very popular and easy games by women and children. These objects could also be used, however, as offerings to a female deity or as a funerary gift, in particular in children’s tombs. Hundreds of astragaloi, part of which were examined in this paper, were discovered among other votive ceramic objects in the cave of Koroneia, located on the north-east side of Mount Helikon.

The site has been identified as the sanctuary of the Leibethria Nymphs and the Nymph Koroneia, the nurse of Dionysos. Figurines are the main kind of object discovered in the cave and their dating ranges from the 6th century BC to the Hellenistic period. Most of the astragaloi collected from the cave were not painted. Only a few of them were coloured, revealing most probably that particular care was given to these objects destined to be offered to the Nymphs.

This paper presents the most significant results of an analytical multi-technique approach for the chemical characterisation of the colour applied on five painted astragaloi from the cave of Koroneia. The main objective was to better understand the painting technique adopted for their decoration and the nature of materials involved in it. Optical microscopy, environmental scanning electron microscopy (ESEM), micro-ATR and FT-IR together with liquid chromatographic techniques were applied to several astragaloi samples. Although hydroxyapatite from bone was the main compound detected in the IR spectra, other absorption peaks suggested the presence of diverse organic substances.

Specifically, the results showed that:
- red and yellow lakes are present as highlighted by both ESEM-EDS measurements, showing that aluminium is the major inorganic element present, and by HPLC analysis from which the red lake is identified;
- red inorganic pigments such as limonite are absent;
- a blue inorganic pigment has been found as a ground for the red lake;
- silicium is present in high amounts in all the samples.

In particular, the paper discusses the kind of lakes found and the presence of Si.
035 Characterization of Decorations and Pitch Paying of the Shipwrecks Found in the Archaeological Site of Pisa Harbour (Italy)

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An archaeological excavation in Pisa (Italy) which began in December 1998, brought to light the remains of a harbour dating back to Etruscan and Roman times. In the course of the excavation several well-preserved shipwrecks were found and some of them still exhibited painted decorations. The reasonably good state of conservation of both the wood and paints was attributed to an anaerobic environment which has lasted over the centuries and to the huge amount of coating material applied to the ships. In order both to characterize the materials employed and to obtain more information regarding their state of conservation, samples were collected.

Analysis by Fourier transform infrared spectroscopy (FT-IR) and gas chromatography-mass spectrometry (GC-MS) was carried out for the characterization of organic compounds. Energy dispersive X-ray microanalysis (EDX) and X-ray diffraction were used for the identification of the inorganic pigments.

The major organic constituents of the archaeological samples discovered were tricyclic diterpenoids based on the abietane skeleton together with linear long-chain alcohols and acids. The EDX-XRD analysis showed that red ochre and kaolinite were employed as red and white pigments over an underlying layer of cerussite. The results, discussed in this paper, suggest that the material used as pitch paying was a pitch obtained from pine wood. Red ochre and kaolinite, over cerussite, bound with diterpenoid resin from Pinaceae genus and beeswax, were used to paint the ships.

036 Contribution of Raman Microspectrometry to the Study of Wall Paintings

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Raman microspectrometry is a technique well adapted to analytical investigation of art works, and more and more applications on this topic are published. One of our fields of research concerns the characterisation of pigments in wall paintings. Usually, the analyses are performed directly on fragments placed on the stage of the microscope. However the analysis of large paintings requires a microsampling.

The results presented here concern wall paintings of ancient and medieval times. Roma and in its whole empire used the same pigments. We have identified a typical Roman blue pigment (Egyptian blue) in sites as far away from Roma as Brittany and Samarkand. There is a large range of red pigments, usually minerals: mercury sulphide, iron oxide, lead oxides, arsenic sulphides. This range also includes an organic product, since we have identified, on a Pompeian sample, an anthraquinone extracted from madder.

A capital of Saint-Denis abbey (France) was painted twice, beginning and end of 12th century, with ultramarine blue then azurite. At Cluny (France), we detect a change in red pigments on two successive painting layers, minium then vermilion.

Some pigments are common, whatever the civilisations, yellow and red iron oxides, carbon black. For the latter, the identification of apatite would indicate that the black pigment is made with burned bone but we never observed the Raman bands of this compound, whatever the origin of the studied samples.
X-Ray Analysis of Medieval Frescoes in Czech Castles and Churches

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A “Laboratory of Quantitative Methods in Monument Research” has been set up at the CTU Prague with financial support from a grant awarded by the Ministry of Education, Youth and Sports of the Czech Republic. Its primary purpose is to investigate historic architecture, although other objects of art can also be a matter of interest. Radioisotope X-ray fluorescence analysis (RXRFA) has been chosen as a useful method for in-situ analyses of various artifacts that are not transportable into the laboratory.

Wall paintings and frescoes in historic buildings are typical examples of such works of art. Quantitative analyses are impossible by RXRFA because of badly defined paint layers, but valuable conclusions can be drawn from qualitative measurements of the presence of certain elements in the paints.

The following monuments of the Czech cultural heritage are among the objects that have been investigated: (i) newly discovered Late Gothic frescoes in the palace and chapel of Žirovnice Castle (Gothic castle from the 13th century in SE Bohemia, rebuilt in the 2nd half of the 15th century, again rebuilt and newly fortified in the 16th century), (ii) frescoes in the Chapel of Our Lady at Karlštejn Castle (Gothic Castle from the 14th century built by Emperor Charles IV, about 15 miles SW from Prague, substantially restored in the 19th century), and (iii) frescoes in the Church of Our Lady before Týn (Gothic church in the Old Town of Prague from the 2nd half of 14th century, with many Baroque supplements).

As Gothic was one of the greatest artistic periods in Bohemia and throughout Central Europe, all these paintings are a highly valuable matter of permanent interest for art historians.

The results enable us not only to differentiate between the old parts of frescoes and the later repainting, but also to gain some information about the types of pigments used by medieval painters. For example, a different type of red pigment was used in Žirovnice according to the importance of the object painted (for less important objects - elements of architecture or ornaments - cheap iron containing mineral pigments from local sources were used; for major saints and benefactors, minium was used; and for the most important objects, e.g., arrays of Jesus and of one of the three Kings, vermilion, which was extremely expensive at that time, was applied).

Roman Frescoes: Characterization and Provenance of Pigments and Plasters

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A wide contest of Roman frescoes constitute the object of a research presently in progress at the Earth Sciences Department of Siena.

The main objectives of the project can be listed as follows: a) the identification of the pigments; b) the provenance of the pigments and the technology related to the their preparation; c) the characterization of the plasters.

According to the stated objectives, numerous frescoes have been sampled in representative archaeological sites like the Roman Forum (excavations on the Palatine Hill, at the Temple of
Concordia and Piazza Iside - Rome), the roman villa of Isera (Trento) and the roman House of Diana at Cosa (Grosseto). Within the same archaeological context, the samples have been selected on the base of the colour of the pigment and the macroscopic distinction observable in the layers of plasters. The characterization of the pigments was obtained with different methodologies both destructive and non-destructive including micro-Raman spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD).

The identification of the pigments has been established mainly through micro-Raman spectroscopy. Analyses of the frescoes revealed eight pigments: vermilion (cinnabar-HgS) and red ochre (hematite-Fe₂O₃) used for the red colours; Egyptian blue (cuprorivaite-CaCuSi₄O₁₀) for the blue colour; yellow ochre (goethite-Fe₂O₃nH₂O) for the tonalities of yellow and clear brown; green earth (celadonite-K(Mg,Fe,Al)₂(Si,Al)₄(OH)₂) and malachite (CuCO₃Cu(OH)₂) for the green colour; Calcite (CaCO₃) for the white and coal for the black.

Provenance investigations have been performed on the cinnabar pigment used at Cosa through the elemental analyser isotope ratio mass spectrometry (EA-IRMS) and provided proof of the spanish origin (Almaden) of this pigment.

The characterization of the plasters has been determined mainly by SEM but micro-palaeontological evidences were further observed. Moreover, the integration of the analytical data with the archaeological sources provides meaningful information on regard of the exploitation of the natural sources, the techniques adopted for the preparation of both pigments and plasters, the economics of the stylistic choices and the diachronic and/or geographical distinctions of the frescoes paintings.

039 The Analysis of Copper Sulphates in Illuminated Manuscripts by Micro-Raman Spectroscopy and the Question of Their Origin?

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Among the various components of ancient painting layers, the green pigments are particularly interesting. In the majority of the literature describing colours materials, two copper greens are commonly cited: malachite, CuCO₃·Cu(OH)₂ and verdigris, Cu(CH₃COO)₂·[Cu(OH)₂]₃·2H₂O. Analyses performed in our laboratory during the last years, have demonstrated that the artists (painters, illuminators, …) in the Middle ages and Renaissance are actually employing more than these two copper greens, in particular various copper sulphates. These copper sulphates can be identified easily from micro-Raman spectroscopy. Indeed, that technique gives us a clear answer on the pigment nature through its molecular spectrum. In addition, it is a non-destructive analytical method (provided some care is taken) allowing the in situ examination of ancient illuminations.

This study has been carried out on illuminated folios belonging to the Art Library of the University of Liège. The most important group of folios originates from the north of Belgium (16th century) and the other folios come from France, Germany, Netherlands and Italy (15th–16th century). To our surprise, most of the green pigments used on these illuminations are sulphates, among which posnjakite is the most frequent. We have then been interested to the question of their origin. Two possibilities can be considered: at first the pigments could have a natural mineral origin and secondly they could have been synthesized from copper sulphate mixed with another component. As far as the mineral origin is concerned, this is in principle possible but the natural deposits are fairly rare in Europe. For the other hypothesis, the principal problem is the lack of recipes corresponding to their synthesis.

In this paper, we shall propose, in particular from Raman spectra, that the most probable provenance of posnjakite was a natural source from a mining in the north of Europe.
**040 Early Italian Renaissance Lead Antimonate Yellow**

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Lead Antiminate or Naples Yellow is one of the most common synthetic yellow pigments in the history of the visual arts. It was used from the 18th Egyptian dynasty (ca. 1500 BC) until about 1850 AD. In its early history the pigment was mostly used as an opacifier of glass and ceramical objects of mid-eastern origin. From about 200 AD to 1100 AD, however, the pigment seems to have found little use. Around 1550 the pigment is suddenly applied in Italian Renaissance oil painting. Titian has been identified as one of the earliest painters to use lead antimonate. However, the circumstances under which Lead Antiminate Yellow suddenly pops up in the Italian Renaissance have not been clarified. Was Lead Antiminate Yellow simply re-invented by the Italians? Or was knowledge on the pigment passed on from elsewhere?

In this presentation a study of two early Italian textual recipes is reported, in which the production of Lead Antiminate Yellow is described. The recipes were subjected to historical, terminological as well as technical examination. Reconstructions of historical Lead Antiminate Yellow were made according to the descriptions of these sources. X-ray powder diffraction (XRPD) was used to examine the reaction products. Our findings throw light on how early Italian Lead Antiminate Yellow was made, which ingredients were used and how the Italians acquired their knowledge on Lead Antiminate Yellow.

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**041 Neolithic–Aeneolithic-Bronze Age (VI-II Millennium BP) Flint Chipped Industry from the NW of Malaga Province (Spain): Raw Materials and Possible Source Areas**

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The valley of the Turón river, a tributary of the Guadalhorce river, is placed at the Northwest of the Malaga province, South Spain. This has been an important area of transit, between the Mediterranean coast and the inland of central Andalucía, along the historic and prehistoric periods. A wide and continuous archaeological register from the Palaeolithic to the Mid Age is present in this valley. This reflects an abundant human occupation of the area.

The project of archaeological prospection in the valley of the Turón river has allowed us to document a register of 24 sites (centres of population, caves, lithic production workshops, necropolis). Archaeometric characterization (optical microscopy, X-ray diffraction and ICP-MS-LA spectroscopy) of chipped siliceous lithic materials from the III-II millennium BC from archaeological settlements in the Rio Turón valley, are carried out.

Mineralogical and petrological features of these materials are compared with the possible geological source areas in this area: flint materials from the limestones and dolomites of Jurassic-Cretaceous age (Subbetic and Betic Units materials, of the Betic Cordillera); and other siliceous lithologies as radiolarites, Tertiary sandstones, etc. that appear in the archaeological register. The flint extraction by quarrying or mining works are linked to the obtention of siliceous materials for the elaboration of tools that will be used later in the domestic diary works, as well as in artefacts production of forest works, as axes, picks, big retouched flakes. They allow us to obtain an important approximation to their catchment and sources.

We developed a technological and typological study of the products as an approximation to the technology and the working processes. Here we carried out a contrast between the various lithologies and the archaeological types, that informed us of the possible preferences associated with the use of the available raw materials.
We have studied a selection of 65 archaeological samples of chipped stone industry from four flint workshops of the III Millennium (La Galeota, Castillo de Turón, Lomas del Infiero and Morenito) and one workshop of the II Millennium BC (La Raja del Boquerón). Other lithic production areas are also located in this valley. A certain specialized production exploitation is kept of the mine and quarries of siliceous materials, for local consumption and to supply the villages of the Guadalquivir valley countryside.

This methodological frame aspires to integrate the geological resources with the archaeological facts. The local and regional knowledge helps to understand the lithic potential resources of this zone.

042 Collar Beads from the Tafí Culture, Tucumán (Argentina), Ist Millennium AD: Raw Materials Characterization and Provenance

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Tafí Culture was developed in the Tafí valley area, Tucumán province, North of Argentina, between 1 and 1000 AD. This culture corresponds with a society with agricultural economy and an advanced knowledge of the irrigation techniques and terrace cultivation. Also they have llama cattle-raising activities.

An abundant settlement of this geographical area was probably produced, with little familiar units distribution, nearby between them. Habitation units are constituted by two or three circular rooms, of 2-6 meters in diameter, around a central circular nucleus of 10-15 meters in diameter.

Archaeological materials are dominated by rough ceramic industry, in general painting in monochromatic red, rarely is polished grey or black. Radiocarbon dating of organic materials in many settlements of this valley shown dates from 1140 ± 50 / 2296 ± 70 BP.

In the excavation of a composed residential unit in El Tolar area, appeared three burials in cist, as substructures under the occupational level. These structures are of cylindrical morphology, with false vault. At the cist number tree, dated at 340 AD, appeared an individual burial present ceramic and a collar with a great variety of beads.

The studied collar was composed of 299 beads of different morphologies and compositions. A selection of 8 beads of the representative kinds of lithologies was analysed.

Optical microscopy, X-ray diffraction and ICP-MS-LA spectroscopy was employed in the chemical and mineralogical characterization of this materials. Different lithologies appear in the beads, cream sandstones, blue and pale green turquoise, green beads of a mica group mineral and brown beads of opal and quartz. Geological features of this region have been studied in an attempt to elucidate the possible source areas for these materials.

The non presence of minerals as turquoise in the local geology suggest a alloctonous provenance for all or a part of these raw materials. The more closets geological outcrops with this mineral appear at the North of Chile, at the other side of the Andes Cordillera.

043 Archaeometric Studies of Prehistoric Pigments and Paints in South Africa

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Southern Africa has a wealth of extraordinary rock art most of which is attributed to the San (“Bushmen”) and their ancestors. It has been estimated that there may be over 20,000 sites in South
Africa alone. Since research commenced in the late nineteenth century, rock art research has progressed from recording and speculation as to its “meaning” to more rigorous studies. Archaeometric studies have tended to focus on the problem of dates, yet the issue of paint composition is a parallel field which has been under-researched. Yet it has clear implications for dating projects, since carbon dating of the paintings depends on the presence of organic materials added as binders. Few scientific studies have been directed towards analysis of the paints (and, by extension, the pigment residues from archaeological deposits). The methods used – XRF, XRD and SEM – remain important, but these studies (especially the first two mentioned) were particularly limited by sample size, and little further work has been conducted. The potential of pigment and paint analysis is nevertheless enormous. On the one hand, knowledge of the constituents of paints provides cultural information about the practice of painting. Various ethnographic reports from the early nineteenth century suggest that every phase of the process, from pigment mining to paint manufacture to actual image production, probably had a magical and/or ritual dimension. In conjunction with further investigation of the sources of pigments, information about trade and/or transhumance may be obtained. From a conservation point of view, an understanding of paint composition (and possible regional variations in paint “recipes”) has the potential for furthering our understanding of processes of deterioration, and, by extension, remedial conservation measures. Last, but not least, an understanding of paint composition has relevance for both absolute dating (which depends on organic components) and indirect dating.

An extensive project involving SEM, TEM, XRF and XRD analysis of red ochres from various areas of KwaZulu-Natal was initiated in 1999. The analysis showed that certain pigment deposits indeed showed distinctive trace elements. In a follow-up study, pigmentaceous waste from excavations in a Later Stone age cave site with abundant paintings was also analysed. This study revealed that the paint samples contained phosphorus (a pointer towards the nature of organic additives to the prepared paints) and that the excavated pigments did not seem to match the paint on the cave walls. It is possible that it is the smaller pieces, of higher quality, that were used for the paint and that the lower quality larger pieces initially analysed relate to other activities. Since both conventional XRD and XRF analyses generally require relatively large samples, numerous pieces of pigment waste, as well as the paint samples, could not be analysed because of insufficient quantities available (in the case of paint samples, because of legal restrictions on the size of sample that can acceptably be taken). This report presents the findings of a pilot study utilising synchrotron x-rays, the advantage being the possibility for fast data collection on minute quantities of material. This approach offers the prospect of surveying a large number of samples for both mineralogical and elemental composition.

044 Investigation of Parchment Paintings Using Transmission Electron Microscopy and Micro-Raman Spectroscopy

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Illustrated manuscripts are a very interesting way to obtain information about the past, not only through their contents, but also by the document in its own right, for analysis using materials research techniques may convey a lot of information about how it was manufactured. In the present contribution a survey will be given of the kind of information that can be obtained when a parchment illustration is investigated using transmission electron microscopy (TEM) and micro-Raman spectroscopy (μRS). A detailed non-destructive investigation of the paint surface can learn which pigments were known and used at the time. However, if samples can be acquired even more information can be obtained, also about the interior of the painting. When the sample represents a complete cross section, including
the parchment as well as the paint, it can reveal the used painting techniques by exposing possible various paint layers and/or preparation layers. For example, when a certain piece has been damaged or is subjected to deterioration, sampling may be considered in areas close to the attacked regions, so that it doesn't show. Cross section samples can help to explain why the appearance of the material is changing or what causes the degradation and thus also how it can be stopped.

When working with samples TEM and µRS are an obvious choice, since they both need little material to work with. Moreover, a combination of techniques is clearly an advantage to acquire as much information as possible and TEM and µRS give complementary information. TEM is a technique that can be used for very detailed analysis of the micro structure and inorganic pigments for it identifies and characterises individual pigment particles and their respective interiors, also if they are smaller than 1µm. On the other hand, µRS can be used to identify inorganic as well as organic pigments. The combination with an optical microscope also allows studying small grains, be it with dimensions starting from and above 1µm.

Examples will be given of investigations of modern equivalent and historical parchment paintings.

045 The Specific Chromogenation of Tissues and Threads with Red Hg-containing Pigment Montroidite on the Ancient Textiles of 3-4th Millenium BC

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Some textile samples from the Moscow State Historical museum collection were studied with aid of various scientific experimental methods.

These threads were not dyed with organic dyes but chromogenized with “paint” containing the red pigment montroidite HgO (very similar to cinnabar HgS) and organic binding media and/or clay mineral binder. The qualitative and quantitative element and mineral content as well as organic binding media and/or clay mineral binder were examined.

046 The Structural Effects of Wood Ash on Lime Plaster

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Lime plasters containing wood ash have been encountered on a variety of ancient hydraulic structures from the Middle East and North Africa. These plasters, characteristically gray in color with particles of charcoal exposed, are common substrates in plaster linings on cisterns and aqueducts from 1800 BC until historical times. Literary references regarding the substrates are scarce however, and little definitive testing of ash-modified lime plaster has been done.

This may result from the common assumption that wood ash is a contaminant fuel residue from manufacture, with negligible or deleterious effects upon lime plaster, and that such plasters are merely low grade materials used in protected applications. The prevalent contexts of such plasters in durable hydraulic linings however, does suggest that wood ash may impart qualities advantageous for this purpose, regardless of whether it originated as a contaminant or was added specifically for this purpose.

This research examines a substrate plaster from the Roman Aqueduct at Caesarea, Israel. Based on this analysis, samples of lime plaster containing wood ash were constituted and tested for performance criteria relevant to plasters, such as water retention, shrinkage, setting time, carbonation, adhesion, flexural strength, and permeability. Results show the addition of wood ash as improving the performance of lime plaster for substrate applications, strengthening the hypothesis that it may have
been intentionally added for this purpose. The possible mechanisms by which organic ash affects lime plaster are discussed, together with its potential for improving lime mortars and plasters for architectural conservation.

047 Technology of Chinese Wall Paintings from the Han and Tang Dynasties

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The province of Shaanxi in Northern China has been the administrative and cultural heart of more than 15 dynasties throughout the Chinese past. Numerous remains of palaces and imperial tombs, such as the burial mount of the Emperor Qin Shi Huangdi (221-210 BC) with the famous terracotta warriors, are spread in the loess planes and the surrounding mountains. The German "Römisch-Germanisches Zentralmuseum Mainz" and the Chinese "Archaeological Institute of the Province Shaanxi" have been co-operating in the field of conservation of historical relics for more than 10 years now. During the last two years beautiful wall-paintings from several tombs dating from the Eastern Han (25-220 AD) and Tang (618-907 AD) dynasties had to be rescued as a result of commercial building activities. In the course of the conservation works on the wall-paintings of a Tang Dynasty tomb near Pucheng and a Han Dynasty tomb near Xunyi, the structure of the different underground layers was investigated, as well as pigments and binding media by XRD, SEM, FT-IR, Raman and other techniques.

In both periods secco-techniques had been used. Due to underground humidity and the decay of the organic binding media the pigment layers have survived in a powdery condition. In some samples only could extremely faint traces of organic remains be detected. A wide range of inorganic pigments such as the Han Blue (the barium copper silicate equivalent to Egyptian Blue) has been identified, but also the presence of some organic colorant was established by Raman spectroscopy. Whereas Tang-Dynasty craftsmen used a very thick layer of loess together with several layers of a coarse calcareous mortar (15 cm altogether) to cover the irregular brick vault underneath, the thickness of the loess layer of the earlier Han-period never exceeded 1 cm and sometimes the colour was directly painted on the bricks. This made the recovery of the paintings according to the distacco-method extremely difficult.

048 Characteristics of Mud Plasters on Hittite Buildings in Sapinuva-Çorum

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The Sapuniva Hittite city was uncovered by the excavations started in 1990. The establishment of the city was predicted to be during the years of 1500 BC. The city has witnessed a fire during which mud plasters and mud bricks were damaged and burned. Therefore, selection of the mud plasters had to be done through the analyses of burned materials which had to be identified as mud plaster, mud brick and soil at the beginning of the study. The study aimed to identify mud plaster technology in terms of raw materials composition and the types of fibrous organic additives such as the type of straw which may have been added directly by chopping or through the addition of herbivorous animals dung. Since the burned material was analysed, the results had to be interpreted for the characterization of unburned mud plaster layers.
The physical and mechanical properties of the plasters were studied by the measurements of bulk density and total porosity using RILEM standard test methods, and ultrasonic velocity measurements. Petrographic properties and mineralogical composition were determined through thin section analyses by an optical microscope, XRD, TGA and SEM coupled with EDX analyses. A stereo microscope was used to examine the impressions of fibrous components in the matrix.

The results were interpreted for the temperature of burning, the type of soil used as main component of mud plaster, the proportions of its components as sand, silt and clay, the origin of fibrous organic additives whether they have been added as herbivorous animal dung. The results were also interpreted for the presence of multiple plaster layers. The physical, mechanical and compositional properties of mud plasters studied were also useful to suggest some conservation treatments for these materials.

049 The Juice of the Pomegranate: Quality Control for the Processing and Distribution of Alumen in Antiquity

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The Aegean island of Melos was well known in antiquity for the industrial mineral (IM) ‘alumen’ as well as sulphur and Melian Earth. While the technology of processing insoluble minerals for pigments and other products must depend mainly on their physical properties, alumen is soluble and it is its chemical properties which were undoubtedly of importance in its processing as well as uses. Pliny (1st Century AD) praised Melian "alumen" and stated that its purity could be tested using pomegranate juice and oak galls.

Our research, which forms part of a project on 'IMs in Antiquity' in the Aegean, is endeavouring to establish the nature, origin and sources of Melian alumen as well as methods used in its extraction and processing. Melian alumen was probably an efflorescent salt, an aluminium-sulphate mineral (alunogen) with variable amounts of K, Na, Mg and Fe sulphates, which formed readily workable deposits at sulphurous fumaroles in the post-volcanic but geothermally active landscape of SE Melos. XRD, SEM with EDAX, ICP-AES, stable isotope analyses and computer modelling of chemical solutions have been used to characterise and understand the origin and properties of the efflorescent salts. We have confirmed that pomegranate juice and oak galls, both rich in gallo-tannic acid, are very effective in detecting impurities, especially iron, thus we are starting to elucidate aspects of what must have constituted “quality control” in the IMs trade in antiquity.

Purification in Roman times, especially for medical applications, could have been achieved by fractional crystallisation in solution using convenient low temperature geothermal energy at Aghia Kyriaki, a coastal site on Melos characterised by an abundance of ‘industrial’ pottery sherds. Our field and laboratory experiments are providing a better understanding of alumen, the "aspirin of antiquity" which had many diverse applications before it became a major industrial chemical in the medieval period. This understanding will guide further surveys for industrial mineral mining sites on Melos, future excavation of processing sites and potential provenancing of Mediterranean alumen.
Synchrotron XRD Mineralogical Analysis of Carthaginian Post- and Ante-Mortem Make-up

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Natural antique colorants include red pigments such as cinnabar and ochre and pink pigments such as madder. They were used as ritual or cosmetic make-up. They are material evidence of handcraft activities, social customs and trade in the Mediterranean. Very small quantities of pigments, still in their sea-shell containers, were found during excavations in the archaeological sites of Carthage, Kerkouane, Bekalta, Bouaoudra and elsewhere in Tunisia.

Ten cosmetic make-up samples from the excavated material, already characterised for elemental composition using AES in Tunisia, were studied with SR-XRD at the Brookhaven National Synchrotron Radiation Source, USA, and at Daresbury Laboratory, UK using very small quantity of material (ca. 2mgr) in thin capillaries. The same capillaries were used at both sites. The objectives were the characterization of these pigments in their archaeological context, the differentiation between make-up used before death (cosmetic) and a make-up used to vivify the dead (replace the dead person's blood) and the creation of a database. Because of the Punic wars with the Romans, there is little material evidence of Carthaginian social customs and beliefs.

Four samples contain cinnabar and quartz while four other samples contain haematite, quartz in ratios varying from 75:25 to 35:65wt% and in one case calcite (10wt%) as major phases. These values were obtained by Rietveld fitting of the high resolution diffraction patterns obtained at NSLS. Area CCD detector data obtained at Daresbury were used for fast (30sec) mineralogical characterisation and quick identification of grain texture and particle size.

The results on these first eight samples are typical of what would be obtained from raw (as mined) materials indicating that they were not subjected to any sophisticated refinement process, other than grinding to fine powder as witnessed by the asymmetric profiles of the quartz diffraction lines. These pigments were used as ritual, post-mortem make-up. Diffraction patterns from two other samples exhibit a strong amorphous background. Preparation required the use of sophisticated techniques for extraction and purification of the plant-derived organic pigment. Weak diffraction lines do not correspond to the JCPDS database pattern for porpurin or other related pigments such as alizarin. Presence of goyazite (strontium aluminium phosphate hydroxide) is possible, probably a by-product of the refinement process.

Investigation of "Gray Flint" Samples with Prompt Gamma Activation Analysis

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Flint is a collective term for shallow-water sedimentary siliceous rocks formed in relatively young (Cretaceous, Tertiary) sediments. In broad sense it is applied for other siliceous rocks of sedimentary origin. Colour, pattern, texture of flint varieties can be specific to sources, however over wide areas the similarities raise more questions in provenance studies. Moreover, it is imperative to find objective arguments supporting long distance trade in some enigmatic instances like the appearance of Prut flint in a distance of 600 kms from the source region at Esztergom-Gyurgyalag. Epipalaeolithic site as dominant raw material of the lithic assemblage.
The main objective of our study was to find non-destructive means for separating sources and finding the provenance of archaeological specimens made of grey flint varieties. Geological samples investigated in this series of analysis were provided from the Lithotheca collection of the Hungarian National Museum from the following localities: Saspów PL (Jurassic Craców flint), Wierzbycza Zele PL (Chocolate flint), Krzemionki PL (Krzemionki flint), Świeciechów PL (Świeciechów flint), Beblo PL (Jurassic Craców flint), Marsovice CZ (Krumlovsky Les type chert), Nagytelel HU (Tevel flint), Prut region RO (Prut flint), Volhynia UKR (Volhynian flint), Maňów PL (erratic flint). All these sources yielded material used in the regional and, partly, long distance supply of raw materials. Comparative archaeological samples from several Upper Palaeolithic sites in Hungary were studied: Nadap (erratic flint), Esztergom-Gyurgyalag (Prut flint), Bodrogkereszttúr–Henye (Volhynian/Prut flint).

Preliminary investigation of three samples were performed at the Institute of Isotope and Surface Chemistry by Prompt Gamma Activation Analysis (PGAA) method. The measurements were done with the new cold (14K) neutron beam of the Budapest Research Reactor, Hungary. The effective neutron flux of the beam was $5 \times 10^{7}$ cm$^{-2}$s$^{-1}$, the typical measurement time was 10.000s. The first results indicate that the method can be efficiently used for identification of grey flint varieties. Above the major component (more than 95% Si) numerous trace elements, for example H, B, Al, Cl, K, Ca, Ti, Mn, Fe, Cu, Cd, Sm, Eu, Gd can be detected, based on which we wish to classify the geological and archaeological samples.

052 Ancient Lime Masonry Mortars for Restoration with Organic Additives

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The monuments built with stones in Central Mexico were bound with lime mortars, different volcanic sands, water and organic additives like cow blood, cactus sap, wool, cotton, eggs, white egg, yolk, milk, milk cream, lord, bee honey and of course the witness samples without additive. Here we studied 12 different admixtures of ancient mortars and the samples studied were elaborated in the Laboratorio de Materiales de la Universidad Michoacana. In all the cases the ratio between the lime and the sand was 1:2, and the water was added until the admixture was in 115% as described in ASTM C 230.

The volcanic sand was an igneous extrusive rock, it was classified like andesite, its silica weight percentage was around 55 %, and it was characterized as specified in the American Society for Testing and Materials (ASTM C 33-2000), with the standards: The andesite quarry stones are very common settlements in Michoacán, where the study was carried because it is located in the middle cross of the Mexican Volcanic Belt, the Occidental Sierra Madre and the Rivera and Cocos Plaques, the particular geography and topography is the origin of the pyroclastic flows, and the andesite stones came from this geological phenomena. The sand was ground until < ASTM No. 400, and the material was analyzed by X-ray fluorescence and X-ray diffraction. The mineral species were andesite, plagioclases and glass or non-crystalline material; it also had phenocrysts into the vitreous matrix.

The samples were elaborated in different sizes like cubes of 2x2x2 inches for the compressive strength, ASTM C109; bars of 2x2x4 inches for the flexural modulus of rupture, ASTM C 78, and briquetas of ¾x2x4 inches for the tensile strength, ASTM C190. The samples were tested at 3, 7, 14, 21, 28, 45, 60 and 90 days aged in all the mechanical strengths in a Universal Mechanical Machine, 150 capacity Ton.
The andesite is an acid stone, $\text{SiO}_2 \geq 55\%$ and the atmospheric environment $P_{\text{H}}$ is 6.0-6.5. The weather is warm, $T \approx 27^\circ\text{C}$, the wind speed is $\approx 3.0\,\text{m/s}$ and the principal winds came from the S, the rain is =.

053 An Application of Raman Spectroscopy to the Study of the Pigments Used for the Fresco Decoration of the Saint George Chapel in Aosta

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A chapel dedicated to St. George is part of the Priory palace attached to the church of St. Orso in Aosta. The ancient medieval Priory was restored and partly rebuilt around 1470, when the noble and wealthy Georges de Challant became the Prior of St. Orso; the chapel, a small rectangular-shaped room on the second floor, was consecrated to his private devotions and entitled, after his own name, to saint George. A painter, whose name remains unknown, decorated it with frescoes representing two scenes from the life of St. George, the Virgin with Child and Georges de Challant kneeling in prayer, the Annunciation, the saints Peter, Orso and Mary Magdalen.

The chapel frescoes are at present under analysis, in view of a restoration project: up to now, non-destructive reflectance measurements and microRaman analysis have been performed with the help of portable instruments, the first aim being that of identifying pigments in the painting layers. Raman spectra were recorded with a Renishaw RA 100 transportable instrument using a 785nm laser excitation line and a fiber optic probe equipped with video viewer. Visible reflectance spectra and colour coordinates were obtained by a Minolta CM508i portable spectrophotometer.

According to the results of these analyses, our artist’s palette is mainly composed of inorganic pigments such as cinnabar, azurite, white lead, carbon black and ochres (red and yellow iron oxide and hydroxide have been identified). Spectra from lead-tin yellow type I are of some interest, since this pigment is known to have been introduced in Italy not before 1440. Lead-tin yellow type I was detected in the chapel on most of the green areas; reflectance spectra suggest that here it is mixed in different proportions with a green or blue pigment (probably azurite) to obtain different shades of green. Raman spectra recorded on yellow, red and grey areas show bands from yellow massicot and red lead together. Some spectra from organic compounds may be tentatively assigned to unidentified anthraquinone lakes.

The degradation of pictorial layers under the action of humidity and water infiltrations from the roof cover is testified by a large amount of calcium sulphate; calcium oxalate has also been detected ubiquitously.

054 Pictorial Uses, Quality and Provenance of Red and Yellow Ochres Applied on Late Classical and Early Hellenistic Paintings from Macedonia, Greece

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Red and yellow ochres represent the most common pigments of antiquity, and are still in use by modern artists as well. The diachronic use of these pigments is certainly related to their chromatic qualities but also to their physico-chemical properties. Natural ochres, limonite, goethite and haematite were used in abundance on Macedonian paintings, in a variety of colours ranging from pale yellow, orange, red, to reddish brown, as their physical and chemical properties make them
particularly convenient for use on mural paintings. In fact, they adhere perfectly well with a lime-based support. They are inert and can thus be easily mixed with other pigments. Furthermore, they present important hiding properties and they assure an excellent permanence. These pigments, easy both to find and to prepare, when mixed either between them or with white and black, offer a very wide range of hues that are essential to the painter for the creation of chiaroscuro effects, while mixed with different pigments, they produce new colours.

This paper discusses on the one hand, the pictorial uses of ochres, revealing the expertise of ancient painters in their manipulation and on the other hand, their qualities and properties based on analytical data obtained through an examination of a subset of approximately 30 samples by XRD and SEM-EDS analytical techniques. Elements regarding the possibility of a local provenance of these materials will also be discussed.

055 Petrographical Investigation of Bronze and Iron Age Casting Moulds from the Collection of the Hungarian National Museum

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This study contains preliminary results of petrographical analyses on bronze casting moulds in the collection of the Hungarian National Museum. Moulds were used for casting bronze objects made of different, mainly natural rocks. Their presence on the archaeological sites in large number indicates metallurgical activity and/or workshops on the settlement.

In the course of the present investigations, some 125 objects were surveyed by macroscopic description and low range magnification. Groups were formed among them and characteristic samples were further investigated in petrographical thin section by polarisation microscopy.

A detailed petrographical analysis of the selected items was performed.

About 75% of all samples were made of sandstone. Most frequent types were fine grained types rich in mica, typically with sparite carbonate cement. The rest of the moulds comprised siltstones, (mainly acidic) tuffs, volcanoclastites, metamorphic schist as well as artificial materials (which can be considered a rough type of ceramics). General features include great porosity. Some pieces with favourable thermal qualities were used several times.

Traces of use sometimes also visible macroscopically were observed in thin section as well, like the formation of secondary porosity (due to large and fast changes in temperature), burning of "alien" pieces of pottery grit, transformation of the glassy matrix (limonitisation and initial biotite formation). Features denoting technology include slip-like crust and the presence of silted rock grit in the artificial materials.

056 The Provenance of “Red Marble” Monuments in Hungary

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“Red marble” (Liassic-Dogger red nodular limestone, ammonitico rosso), which has been mined as beloved decorative-stone (Gerecse-Mountains Hungary, Adnet Austria, Verona Italy etc.), has played an important role in the art of Middle Europe and Hungary during the Middle Ages. The provenance of the “red marble” monuments is not feasible only on the strength of petrographical methods, because the two most typical Middle European “red marble” occurrences (Gerecse-Mountains Hungary, Adnet Austria) belong to the same geological age and environment (except some local and typical ammonitico rosso types in Adnet).
The potential sites of extraction of the raw material have been chosen according to geological and historical literatures. These places are: the “red marble” quarries in the Gerecse Mts. (Hungary) and the quarries near Adnet (Austria). 32 samples have been taken from the quarries in the Gerecse Mts. and Adnet, further 27 samples from Hungarian and Transylvanian historical monuments (Sopron, Visegrád, Esztergom, Gödöllő, Pécs, Ellésmonostor, Szermonostor, Gyulafehérvár). Most of the monuments were tombstones and architectural fragments.

The samples from extraction sites and Hungarian and Transylvanian historical monuments have been analysed employing standard petrographic and stable isotope geochemical methods. Based on their $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$ values we could distinguish the material of the Hungarian (1.4 to 2.8‰ $\delta^{13}C_{VPDB}$ and -1.1 to -2.7‰ $\delta^{18}O_{VPDB}$) and Austrian (2.2 to 3.2‰ $\delta^{13}C_{VPDB}$ and -0.7 to 0.2‰ $\delta^{18}O_{VPDB}$) “red marble” quarries.

With these methods we also could determine the provenance of the material used to construct the monuments:

From the 12th to the 16th centuries the raw material of the monuments from Visegrád, Esztergom, Pécs, Ellésmonostor, Szermonostor and Gyulafehérvár was obtained from Gerecse Mts. (Hungary).

From the middle of the 16th century to the 18th century the “red marble” of the Austrian quarries (Adnet) was used in place of the Hungarian raw material. This process is well observable in the case of the archaeological objects from Sopron.

The raw material of the Grassalkovich cinerarium came from Austrian (Adnet) “red marble” quarries and not from Hungary as postulated previously.

The results are in accordance with several historical theories, but in many cases we could give new information about the spreading of this important artistic material.

057 Investigation of the Anatolian Ancient Marble Quarries with EPR Spectroscopy: Expansion of the Data Base

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A large number of samples from the most important marble quarries of Anatolia: Ephessos, Aphrodisias, Afyon (Dokimeion) and Usak (Akmonia and Temenothyrai) were analysed. These quarries are known to have been used in Antiquity, some of them producing large quantities of marble especially in the Hellenistic and Roman times.

The samples were examined under an optical microscope and analysed with Electron Paramagnetic Resonance spectroscopy. The Maximum Grain Size along with a range of EPR parameters, such as the intensities and peak widths originating from the Mn$^{2+}$ and Fe$^{3+}$ ions in the marble crystal lattice and in the accessory minerals, as well as other peaks due to marble crystal lattice defects were measured. The results were amalgamated into the databank of the Laboratory of Archaeometry, NCSR "Demokritos" that includes samples from other known ancient greek marble quarries: Pentelikon, Hymettus, Naxos, Paros, Thassos and Proconnessos in Anatolia. The overlapping of the parameter fields between certain old and new quarries which occurred due to the introduction of a large number of new data in the database, required new approaches to be developed which lead to the selection of new parameter combinations for maximum quarry discrimination.

The new approach with the expanded database was applied to specific archaeological problems.
058 Brazil Lake: Discovering a Main Component of Late Medieval Illuminators’ Palette

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We undertook a few years ago a detailed study of the miniatures of the Boucicaut Master, one of the main parisian illuminators of the beginning of the XVth century, by means of non destructive methods: visible diffuse reflectance and X-ray fluorescence spectrometry. The aim of the research program was to determine the precise illuminator’s palette and to uncover his technical habits. Three illuminated manuscripts were at first considered in situ: the book of hours of the maréchal de Boucicaut, dated ca. 1408 (Paris, Musée Jaquemart-André, ms. 2), the breviary of a dauphin in Châteauroux, before 1415 (Bibliothèque municipale, ms.2) and a Bartholomeus Anglicus in the Bibliothèque nationale in Paris, after 1415 (ms. Fr. 9141).

The abundant use of a red organic dye extracted from brazilwood was amongst our most interesting discoveries. Although in the context of medieval painting, madder and kermes are more frequently thought of, they were totally absent of the palette of this artist. It appears therefore that the use of brazil-lake has been so far underestimated. This supposition is supported by the fact that the medieval technical treaties supply many more red and rose lakes with brazil as chief element than with any other known organic colorant.

We draw our inspiration from these recipes to manufacture in the laboratory different kinds of brazil reds and roses. Some proved to be congenial with the opaque rose surfaces and others with the red translucent glazes we encountered in the miniatures. This evidences the role played by the choice of ingredients which took part in the making of the lake or which were added to it in obtaining the final shade. We extended the scope of our study to examine the importance and ways of use of these brazil-lakes in the miniatures of other illuminators of the same period, including the Bedford Master. We are thus able to propose a more comprehensive view of the question with new scientific results.

059 A Seven Nozzles Stone Oil Lamp with Jewish Symbols from Judea, Israel

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The material culture of the second Temple period in Jerusalem during the first century CE, was marked by the mass production of stone vessels, initiated by the Jewish purity religious laws. A rare oil lamp made of chalk with a double looped handle and seven nozzles, spaced equally in a circle, was studied typologically as well as geologically. The lamp was carved by the drilling wheel technique, as step like marks characteristic to slow speed lathe were left inside the reservoir and the wick holes. Its diameter is 22cm, its height is 6.7cm with a volume of 800cm³.

The flat shoulders that encircle the eye of the oil lamp is carved in a full relief pattern by Jewish symbols of the seven branches Menorah, and the Shiv’at Haminim (Deuteronomy, 8:8). The palm tree with two bunches of dates - the symbol of honey, situated opposite to the Menorah. To its left, clockwise, a vine leaf combined with grapes, two branches: of olive and a ear of barley. To the right of the Menorah, ear of wheat, a shallow braided basket with figs, and three pomegranates hanging from a branch. We suggest, according to the artistic style of most of the symbols, that the oil lamp was produced before the destruction of the temple in 70 CE.

The stone oil lamp is made of hard chalk, belong to the lower part of the Senonian sequence, probably originated from a quarry near Jerusalem. The stone is made of re-crystallized chalk, composed of silicious carbonate (10% SiO₂) with crystals of 2-40 microns in size. Nevertheless, this is a good rock
type for carving and drilling, attaining isomorphic physical strength, up to 32Mpa (Mega-Paskal) for uniaxial stress. The examination of the multi layered patina, reveals composition identical to the oil lamp, but less compact. In addition, a brown encrustation of Rendzina soil, indicating weathering under long burial conditions. We may have here a remarkable important work of Jewish art from the Second Temple period.

060 **Identification of Green Pigments of Gothic Altarpieces by Synchrotron Radiation**

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Identification of pigments, binding media and their alterations belonging to the 15\textsuperscript{th} century Jaume Huguet altarpieces was performed by means of Fourier transform infrared spectroscopy (FTIR), optical microscopy (OM), scanning electron microscopy (SEM) with EDX and conventional wide angle X-ray diffraction (WXRD).

Although the green pigments were determined to be copper compounds, the exact nature of these compounds was not identified. The small size of the samples (below a square millimetre) available, the poor crystalline nature and the presence of a complex mixture of compounds were the main reasons for this. Old treatises indicate that some old chemical procedures for obtaining copper based green pigments could produce a mixture of copper salts (acetates, chlorides, carbonates, etc.). The high penetration, high intensity and low spot size (about 100 square µm) synchrotron radiation allowed to perform a 2-D map of phases of polished thin sections of the paintings.

We present the results obtained on the identification of the green pigments and alterations and their implications on the painting technique and the level of technological knowledge of one of the most important Catalan gothic painters.

061 **Comparison among Different Plaster from S. Abbondio Cloister in Como (Italy)**

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S. Abbondio is an important Romanesque Basilica located in Como (Italy). Its Cloister displays Cinquecento architecture, even if it was partially rebuilt in the Nineteenth century. Nowadays it is object of a complete conservation work and on this occasion a complete analytical survey on plasters, both internal than external, was carried out. Aim of this work was the comparison among plasters coming from different areas of the building, in order to clarify the history of the Cloister and to associate the plasters to the different buildings phases.

Plasters were sampled from architectural elements supposed to be dated to Romanesque, Renaissance and Nineteenth century periods and compared by the morphological, chemical and physical points of view. The finishing layers and the stratigraphy of plasters were as well investigated.
The samples were characterised by means of X-ray diffraction of powders, porosimetric analysis, thin sections observations and Inductively coupled plasma-Optical Emission Spectroscopy. The data supplied a criterion to group samples with similar properties (such as the presence of cement as a binder) which presumably dated to the same period. The results confirmed the historic hypotheses about the sequence of the building interventions, showing how this kind of analytical investigation is a valid support in conservation problems.

062 Sources of Raw Materials for 9th Century BC Glasses from Hasanlu, Iran

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Our lack of knowledge of glassmaking technology during the transition between the Bronze and Iron Ages lies partly in the small amount of well-excavated glass artifacts. One site that has produced a range of suitable material is Hasanlu in northwestern Iran, excavated by Robert H. Dyson, Jr., from the University of Pennsylvania. The archaeological artifacts from the Iron Age Period IVB levels of Hasanlu are unique because of the scarcity of materials from this period and this region. Electron microprobe analysis of unaltered areas of the Hasanlu glasses yields compositions of about 17-22 wt% Na₂O, 2-9 wt% CaO, 0.7-5 wt% K₂O, and 0.8-7 wt% MgO, broadly similar to other Bronze and early Iron Age glasses. Most of the Hasanlu glasses in this study have compositions consistent with the use of plant ash, although a few of the compositions are consistent with the use of mineral soda (natron). There are indications that some Hasanlu glasses were made using similar raw materials and manufacturing practices, and are perhaps the products of one factory or one region in which the same raw materials were procured and processed.

This paper will present the results of trace element analysis using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). These results will be used to confirm or refine the compositional groups tentatively identified from the electron microprobe results. The trace element data, in conjunction with the major element data and archaeological evidence, will also be used to infer the geologic setting of the alkali and silica glassmaking raw materials used for the Hasanlu glasses. The metal colorants that were used to color these glasses will have carried into the finished glass the chemical signatures of the their mineralogical or industrial source. Correlations of colorants with trace elements will be used to interpret what types of ores or processed metals were added to glass batches to yield color.

063 Comprehensive Source Analysis and the Socioeconomic Role of Obsidian Trade in Northern Italy: New Data from the Middle Neolithic Site of Gaione

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The precise geological provenance of the entire assemblage of obsidian artifacts recovered from the Middle Neolithic site of Gaione in northern Italy was determined and provides new insights into the socioeconomic role of obsidian trade in this region. While geochemical fingerprinting of obsidian sources was first applied in the Mediterranean region nearly four decades ago, a detailed understanding of the sequence of behaviors responsible for the acquisition, transport, manufacture, and use of obsidian was limited due to incomplete documentation of the obsidian sources and, until recently, the small number of artifacts analyzed from datable archaeological contexts. Whereas earlier
provenance studies in Italy usually attributed obsidian artifacts to one of four island sources - Lipari, Palmarola, Pantelleria or Sardinia - recent field investigations and laboratory analysis have located and characterized discrete subsources on each island. At the same time, the development of non- or minimally destructive, and less expensive analytical techniques has permitted the analysis of significant numbers of artifacts so that statistically meaningful patterns of obsidian source utilization may be determined.

In 1990, Ammerman and colleagues reported that obsidian from Sardinia, Lipari and Palmarola was present among the 17 analyzed artifacts from Gaione. At the time this was the most samples analyzed from a single site in northern Italy, and the presence of obsidian from three island sources at a single site was also rare. We report here on the analysis of the remaining 82 artifacts recovered from this important site, and reinterpret the original 17 attributions in light of the more detailed source information now available. Following the high-precision measurement of density and a visual estimation of source, the Gaione samples were analyzed by laser ablation ICP mass spectrometry at the Archaeometry Laboratory of the Missouri University Research Reactor. This technique was selected because it provides quantitative results for a large number of trace elements in a virtually non-destructive manner. The results for Gaione are compared with those available for other Middle Neolithic sites, and differences in source utilization are interpreted in terms of geographic location, transport methods, exchange mechanisms, and sociocultural factors. The comprehensive analysis of obsidian artifacts from Gaione also illustrates how mis-interpretations are likely to occur when based on small numbers of analyses.

Reference

064 Identification and Characterization of the Obsidian Sources on the Island of Palmarola, Italy

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The recent geoarchaeological investigation of the small island of Palmarola has led to a more complete identification and characterization of the obsidian sources found there. Located about 35km from the Italian mainland, Palmarola was an important source of this raw material during the Neolithic period, ca. 6000-3000 BC, with artifacts of Palmarola obsidian already identified at archaeological sites throughout the Italian peninsula. While previous research produced K-Ar and fission-track dates and chemical analyses on obsidian from Monte Tramontana at the northern end of the island similar to those obtained on a limited number of artifacts from Italian archaeological sites, apparently no samples from Punta Vardella near the southeastern tip of the island have been dated or chemically analyzed although abundant secondary deposits of obsidian had been reported there. Some variation in the fission-track dates also suggested the possibility that more than one eruptive event was responsible for the obsidian exploited in antiquity.

A detailed survey of the island was conducted in 2000 and 2001, with the permission and assistance of the Soprintendenza Archeologica di Lazio. The survey involved systematic walking and collection along the coastlines, snorkeling to collect samples from nearby islets and areas submerged due to post-glacial sea level rise, and scaling the mountainous peaks of the interior of the island. Several hundred samples of workable obsidian were collected primarily from secondary deposits both at Punta Vardella and along the southwest flank of Monte Tramontana. Only devitrified obsidian of unworkable quality or of small size was found in situ anywhere else on the island. A small amount of
highly transparent obsidian was found at Punta Vardella, but most of the material found in both localities is grey to black and nearly opaque. High precision density measurements were made of all samples, while complete chemical characterization of the Palmarola sources was obtained using X-ray fluorescence, instrumental neutron activation analysis, and laser ablation ICP mass spectrometry at the Archaeometry Laboratory at the Missouri University Research Reactor. These results indicate the presence of at least two distinct sources on Palmarola, allowing more precise provenance determination of obsidian artifacts from archaeological sites in Italy. This will allow greater understanding of the practical and cultural factors involved in the exploitation of this important resource.

065 Archaeometrical Applications of Raman Spectroscopy: Pigment Identification and Beyond

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During the last decades, Raman spectroscopy has become more powerful and has been used more widely, not only for academic or industrial applications, but also for archaeometrical research. Molecular Raman spectra have in general well-resolved bands, simplifying the spectral interpretation and identification of the compounds. Moreover, the speed and the non-destructive character of the method is of high interest to archaeometrists. By using micro-Raman spectroscopy, a high lateral resolution (typically down to $\mu$m) can be achieved, thus minimizing interferences from other compounds in mixtures.

Pigment identification with Raman spectroscopy can easily be done, by recording the spectra and comparing them with those in an established spectral library on pigments. This kind of research has been performed, among others, for oil paintings, mediaeval manuscripts and Egyptian burial masks and is of high interest to (art-)historians, keepers, conservators, etc. These examinations can provide new insights on working methods and cultural interactions. Other possible reasons for pigment analysis might be dating the artefact or finding indications for forgeries.

Raman spectroscopy, being a molecular spectroscopic method, also can provide information on natural organic substances in historical materials. Spectra have been recorded for different types of resins and binding media and interpreted in terms of molecular composition. Also the organic supports, such as parchment, can be studied using Raman spectroscopy. Next to these materials, also reference spectra of organic plant colorants will be presented, as these can serve for future identification purposes.

066 Compositional Analyses of Archaeological Materials Using a Non-Destructive Portable Spectrometer

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A team at the University of Illinois is employing a shoebox-size PIMA (Portable Infrared Mineral Analyzer) spectrometer in provenance studies of stone Cahokia "red goddess" figurines and Hopewellian pipes recovered from sites in the Midwestern United States. The data from this totally non-destructive method for determining mineral composition support earlier analyses by X-ray diffraction (XRD) and sequential acid dissolution-inductively coupled plasma (SAD-ICP) and confirm pipestone sources close to the artifact find-spots (Missouri for the figurines and northwestern Illinois for the pipes).
The combined results are forcing archaeologists to reevaluate raw material procurement, artifact production, and redistribution for the Middle Mississippian (ca. AD 1000-1400) and Middle Woodland (ca. 50 BC-AD 250) periods. PIMA spectroscopy has also proven useful for characterizing low-fired ceramics containing little or no temper, and distinguishing restoration materials (plaster, shellac, etc.) from original components. The PIMA’s advantages (portability, speed, and non-destructiveness) make it a valuable addition to the archaeometrist’s arsenal of analytical techniques, most of which are laboratory-based and require some degree of destructive sampling.

067 Quantitative Fabric Analysis (QFA) and Fractal Analysis (FA) on Marble from Central Europa and West-Anatolia

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Provenance studies of white marble artefacts and building materials have long been a key research topic in archaeometry. In combination with well-known techniques, like trace element determination, $\delta^{13}$C- and $\delta^{18}$O- stable isotope ratios, $^{87}$Sr/$^{86}$Sr isotope ratios, cathodoluminescence investigation, the Quantitative Fabric Analysis (QFA) and Fractal Analysis (FA) are new powerful methods for fingerprinting white marbles.

The grain boundaries of more than 80 thin sections have been enhanced by a manual graphic technique; these images have been scanned and processed in an automated manner to extract the grain boundaries in vector format. This dataset has been analysed with various techniques.

In additional to the conventional grain size determination, we computed the statistical distribution (histogram) of other grain-size-properties, like axial difference (long axis – short axis), ratio perimeter/surface, shape factor, and bifurcation angle pattern.

Fractal Analysis (FA, mass dimension method) has been used to extract pattern related parameters in order to characterise the different samples. Combined with classical analytical methods, the numerical grain boundary pattern evaluation is found to be useful tool in differentiation of West-Anatolian, Austrian, and Slovenian marble samples to clarify archaeological provenance problems in Central Europa and in Troy/Turkey.

068 Provenance Studies on Roman Marble Fragments in the Hungarian National Museum, Budapest

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During the archaeological excavation of the Roman military fortress Heténypusztta (SW Hungary) 860 marble fragments were found, used in a secondary manner for the construction of the Late Roman fortress. Heténypusztta used to belong to the province Pannonia Valeria. The marble fragments originated most probably from memorial stones of a heathen cemetery. The fragments are now in the collection of the Hungarian National Museum. This study is the first large-scale effort for the determination of the origin of marble of Roman period from the territory of Hungary.

More than 80 samples from several Austrian, Slovenian and Macedonian marble quarries, crystalline limestone of marble-like quality from Hungary (Polgárdi Limestone) and so far 18 samples from archaeological objects were investigated. In order to determine the origin mineralogical (by X-ray diffraction), petrographical (by thin sections), stable isotope geochemical (C and O), and cathodoluminescence methods were applied.
Two groups of archaeological objects are distinguishable based on their stable isotope compositions. After comparing with the C- and O-isotope values of the quarries, one could see that the first group ($d^{13}$C = 0.2 to 1.5‰ and $d^{18}$O = -12.3 to -13.6‰) probably belongs to the marble quarries Puppitsch/Kraig ($d^{13}$C = -0.5 to 3.1‰ and $d^{18}$O = -11.6 to -16.2‰) or Tiffen ($d^{13}$C = -1.2 to 0.8‰ and $d^{18}$O = -13.6 to -16.3‰) in Austria/Carinthia. The second group ($d^{13}$C = 0.0 to 2.3‰ and $d^{18}$O = -5.8 to -9.8‰) seems to be derived from the Gummern ($d^{13}$C = -0.1 to 1.9‰ and $d^{18}$O = -4.5 to -10.1‰), Sekull ($d^{13}$C = 0.3 to 1.2‰ and $d^{18}$O = -7.8 to -13.1‰), Treffen ($d^{13}$C = -0.2 to 3.5‰ and $d^{18}$O = -4.5 to -7.8‰) group (Austria/Carinthia). However some samples also overlap with Polgárdi (Hungary) ($d^{13}$C = 0.8 to 2.1‰ and $d^{18}$O = -5.8 to -10.1‰) and Slovenska Bistrica (Slovenia) ($d^{13}$C = -0.1 to 0.8‰ and $d^{18}$O = -6.5 to -8.5‰). More specific reference to provenance will be made by evaluation of petrographical and cathodoluminescence results, and additional isotope analysis both from geological and archaeological objects.

069 Provenance of the White Marble Building Stones in the Monuments of the Ancient Troy

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This study presents the first results of archaeometrical research on marble building material of Troy/Turkey. The building material could have been shipped from various quarries since the marble from which the monuments and buildings could have been constructed have widespread occurrences in Asia Minor. In order to clarify the provenance a systematic sampling and investigation of marble from the Biga peninsula and other Anatolian occurrences was carried out. The first step in the attempt to determine the origin of marbles was the identification and characterisation of the marble materials. A comparison of mineralogical and geochemical characteristics of the Trojan marble monuments with those of local and regional marble quarries there allows a distinction between locally (surrounding area of Biga peninsula) and imported marbles from Asia Minor or other ancient marble production centres, e.g. Aegean islands or Attic mainland.

Several scientific methods were applied in order to distinguish antique marble quarries. No single technique allows clear characterisation of white marbles. Therefore, a multi-disciplinary approach is more promising. As a basic grouping of samples macroscopic features like colour and smell and microscopic properties like texture, grain size analyses and staining techniques were used. The mineral composition was determined by XRD (X-ray diffraction) and microprobe analysis. The variance and Fourier method was applied to determine the changes in coherently scattering domain size and lattice distortion in calcite of marble samples. The domain size and lattice distortion can be applied as a good parameter to characterise the structure of calcite and metamorphic grade. Furthermore, the determination of minor and trace elements was carried out with chemical techniques like XRF (X-ray fluorescence) and ICP-MS (Inductive Coupled Plasma Mass Spectrometry), the $^{18}$O/$^{16}$O and $^{13}$C/$^{12}$C ratios were measured with a mass spectrometer. Finally, for the fine division of samples that were still ambiguous cathodoluminescence and Sr-isotope analyses were used. In summary we conclude that the majority of marbles used for construction of the Trojan architectural elements is derived from Marmara and/or Orhangazi areas, with minor percentages of other northwest Anatolian and Greek shipment at various historical periods.
Recent papers in Technology of Knapped Stone. Papers. People. While the dagger Mistřice II is the undisputable example of northern production, the artefact Mistřice III is, as for technology and material, positively product of a manufacturing area in Lower Bavaria. Save to Library. Download. Chert Source Provenance Studies. Follow Following. Stone Industry. A pigment is a colored material that is completely or nearly insoluble in water. In contrast dyes are typically soluble, at least at some stage in their use. Generally dyes are often organic compounds whereas pigments are often inorganic compounds. Pigments of prehistoric and historic value include ocher, charcoal, and lapis lazuli. In 2006, around 7.4 million tons of inorganic, organic and special pigments were marketed worldwide. estimated at around US$14.86 billion in 2018 and will rise at over 4.9 Along with improved lithic technology, particularly stone-tipped weapons, and a more diverse economic strategy suggested by the faunal remains, larger-scale social relationships would have provided a buffer against increased climate variation and resource unpredictability (34, 39, 40). In a Kalahari environment comparable to that implied by the BOK sites, fauna, isotopes, and other indicators (34), modern hunter-gatherer families maintain contacts with exchange partners up to a 100-km distance but generally range over only a 20-km radius annually (39). Early human use of marine resources and pigment in South Africa during the Middle Pleistocene. Nature 449, 905–908 (2007). doi:10.1038/nature06204 pmid:17943129. OpenUrl CrossRef PubMed Web of Science.