

CONCORSO PUBBLICO, PER ESAMI, A N. 1 POSTO DI CATEGORIA D POSIZIONE ECONOMICA D1, AREA TECNICA, TECNICO-SCIENTIFICA ED ELABORAZIONE DATI, PER LE ESIGENZE DEL DIPARTIMENTO DI SCIENZE DELLA TERRA, DELL'AMBIENTE E DELLE RISORSE (DSTAR) DELL'UNIVERSITÀ DEGLI STUDI DI NAPOLI FEDERICO II (COD. RIF. 2001) INDETTO CON DECRETO DEL DIRETTORE GENERALE N. 437 DEL 30.06.2020 E PUBBLICATO SULLA G.U. IV SERIE SPECIALE – CONCORSI ED ESAMI – N. 53 DEL 10.07.2020

GRUPPO DOMANDE ESTRATTE PROVA ORALE DEL 24/09/2020

- ✓ Vantaggi e svantaggi della tecnica FTIR per la individuazione di fasi mineralogiche della famiglia degli amianti.
- ✓ Procedure di preparazione di un campione per le analisi in XRF.
- ✓ Analisi non distruttive per le indagini in un sito archeologico.
- ✓ Software per l'analisi mineralogica quantitativa di un campione di materiale vulcanico (tufo zeolitizzato).
- ✓ Le potenzialità dell'analisi colorimetrica nello studio dei Beni Culturali.
- ✓ Procedure di separazione di una frazione argillosa mediante sedimentazione e centrifugazione.
- ✓ Utilità delle prove di invecchiamento artificiale in camere climatiche.
- ✓ Software per l'identificazione qualitativa della composizione mineralogica di un campione.
- ✓ Quali sono le potenzialità nel campo dei Beni Culturali delle analisi in DRX?
- ✓ Differenza nelle procedure di preparazione del campione per analisi DRX qualitative e/o quantitative.
- ✓ Il DM 6/9/1994 nella caratterizzazione di un sito potenzialmente contaminato da materiali contenenti amianto.
- ✓ Utilizzo di diagrammi classificativi per la nomenclatura delle rocce lapidee.

PER ORDINE DEL PRESIDENTE
IL SEGRETARIO DELLA COMMISSIONE
F.TO dott. Pasquale PIROLI

3.3 Pigments

Colour is one of the most fascinating properties of matter, as testified by the very early use of pigments in prehistoric paintings, the importance of surface decoration in artwork and everyday objects, and the widespread use of colourants in ancient and modern cosmetics. The physical origin of colour is nested in the absorption and interference phenomena and it has been briefly treated in Section 2.6 and Box 2.f. The measurement of colour is described in Box 3.e. Organic dyes are treated in Section 3.7.5. It is worth remarking on the difference between pigments and dyes: pigments are finely divided insoluble materials that act as colouring agents when dispersed in a medium such as water as in watercolours, oil as in oil paintings, or a number of other organic media (Gettens and Stout 1942). Dyes, on the other hand, are soluble organic complexes that cannot be used alone, rather they are used as colourants of white or colourless particles, such as clays. The substance made by the dyed particles is called the lake.

The analytical and conservation issues related to inorganic pigments will be reviewed here, the most fundamental and practical being: (1) what is the physico-chemical nature of the material?, (2) how is the pigment included or bound in the paint layer?, (3) is it in the original state or is it undergoing alteration?, and (4) what are the strategies to stop deterioration and to stabilize it?

Pigment analysis is a fundamental aid to art history, authentication, and conservation management. Of course colour has so many aesthetical, philosophical, and anthropological implications that the materials science side is just a starting point in the broader colour science (see for example *Technè* no. 9–10 (1999) and no. 26 (2007)). The emphasis here will be confined to basic pigment investigation and methods.

Pigment identification and characterization

The analytical techniques for identification of crystal phases described in the volume are mostly used to answer the first two diagnostic questions. Inorganic pigments have a definite chemical composition and crystal structure, so that they may be identified by chemical analysis (SEM-EDS, EPMA, XRF, AAS, OES, MS, LIBS), by diffraction (XRD, ND), and by molecular spectroscopy (IR, RS).

XRD and Raman scattering (RS) are possibly the most used techniques for pigment identification, because of their sensitivity for crystallographic structure types, molecular environment, and structural polymorphs. Both techniques are so widely employed that several experimental databases of reference compounds are available (Bell *et al.* 1997, Hochleitner *et al.* 2003) for identification purposes. The analyses are generally performed on microsamples of pigment material analysed in the laboratory. Raman scattering has the obvious advantage that it can also be performed in situ in totally non-invasive mode (Smith *et al.* 2000, Smith 2006), though serious attempts are being made to make XRD portable too (Box 2.r). Non-invasive in situ investigation of pigments is of course a critical analytical issue, since any sampling or alteration of the sample during the analysis compromises the nature and appearance of the object. Furthermore,

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the Centro-Camuno di Studi Preistorici, Italy and now co-operating with the Swedish RockCare project (Swedish Archive for Rock Art Research, http://www.rockartscandinavia.se/uk/news/swedish_archive_english.htm) based at the Tanums HällristningsMuseum; the Rock Art Archive at the University of California, Los Angeles based at the Cotsen Institute of Archaeology (<http://www.ssenet.ucla.edu/iaa/rockart/>); the Rock Art Research Institute based at the University of Witwatersrand, South Africa (<http://web.wits.ac.za/academic/science/geography/rockart/>); The Australian Rock Art Research Association based in Victoria, Australia (AURANET, <http://mc2.vicnet.net.au/home/aura/web/index.html>); and many others.

For in-depth information

Clottes J. (2002) World rock art. The Getty Conservation Institute, Los Angeles.
Updated list of Rock Art organizations through the world: <http://www.rock-art.com/orgs.htm>

3.1.2 Structural clay products, ceramics

Modelling wet clays into different shapes was a very early human activity, possibly developed independently several times in prehistory. In a number of European Palaeolithic caves the ancient designs are also traced into wet clays, other than painted on the walls. The French site of Tuc d'Audoubert preserves two moulded but unfired bison shapes (MacCurdy 1912). The earliest evidence of terracotta figurines hardened by fire is the remarkable statuettes of the Gravettian site of Dolní Věstonice, Czech Republic, including the famous Venus (Vandiver *et al.* 1989). At this site well-modelled shapes of animals and humans were expressly inserted in the fire when still wet, possibly to produce an explosive tribute to the gods (Soffer *et al.* 1993). Thermoluminescence dating of these samples produced dates close to 30ky BC (Zimmerman and Huxtable 1971). Another very early figurine dated to about 17ky BC has been found in a rescue operation at Maina, Russia (Vandiver and Vasil'ev 2002). Although very fragmentary, this evidence shows that the Late Palaeolithic humans recognized that wet clay was plastic, it could be shaped, and it retained its form when dried or fired. The basic properties of clay materials were thus already known.

The earliest evidences of the use of fired pottery made of earth materials for everyday tools are in China (Yuchanyan and Miaoyan sites, dated to 14.5–13.8ky BC; Zhao and Wu 2000), Japan (Incipient Jomon period, dated to about 14.5–13.5ky BC; Habu 2004), Russian Far East (Amur River Basin, dated to 14.1–12.8ky BC; Kuzmin 2006) and Siberia (Ust-Karenga 12 site, dated to 12.5–10.5ky BC; Kuzmin and Vetrov 2007). Given the chronology uncertainties, it appears that fired ceramics appeared almost simultaneously in several places in Eastern Asia at about 14000y BC.

The appearance of pottery vessels that were used to contain and store food is generally associated in Europe and the Near and Middle East to the Neolithic changes, involving the adoption of food production vs collection, and living in permanent settlements vs. temporary camps. Although there is no evidence of strict causal relationship between the rise of agriculture, the settlement into

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silica-based materials treated at high temperature, commonly composed of a glass matrix and several crystalline phases, they are mostly used for surface finishing and impermeabilization; *frits* are intermediate highly heterogeneous glass materials produced by melting and air-quenching, they are commonly re-ground and used as base materials to produce glazes and glass.

Slips and *engobes* are particular types of clay-rich coatings generally applied directly on the surface of the ceramic body or in-between the body and the true-glaze layer. Their application is meant to enhance surface adhesion, hide defects, and improve colour-saturation effects from the pigments embedded in the glaze. Red slips are generally made out of fine Fe-rich clays, whereas white slips are made of kaolinite-rich clays. Slips and engobes alone improve the aesthetic quality of the object, but they do not affect the permeability.

3.1.2.4 Characterization methods and interpretation

The investigations of archaeological ceramics tend to answer primarily the three basic questions of archaeometry: how, when, and where was the material produced? Once this starting information is safely obtained, more far reaching inferences may be deduced (Kingery 1981).

How?

The firing processes can be reconstructed from the characteristics of the final product. For example, if the surface is vitrified or glazed, temperatures above 900 °C must have been achieved. High temperature minerals in the ceramic matrix (gehlenite, cristobalite, mullite, anorthite) are also indicative of the maximum temperature of firing. The original temperature can also be assessed by re-heating the ceramic fragments under controlled conditions, and by monitoring the triggering of mineralogical or microstructural changes (Kingery and Frierman 1974).

The use of combined mineralogical and petrographical tools is essential in the characterization of ceramic bodies. A common sequence of analysis includes (a) the mineralogical and petrographical analysis by optical microscopy in a thin section, (b) the mineral phase identification by X-ray powder diffraction, (c) chemical analysis (by XRF, NAA, AAS, OES, etc.), (d) chemical mapping (by EPMA, SEM-EDS, etc.) and (e) the use of spectroscopic tools to evaluate the valence state of oxidizing cations (mainly Fe by Mössbauer spectroscopy).

The optical microscopical analysis on a thin section of the materials allows one to directly evaluate the main phases present in the temper, the approximate filler to matrix ratio, and the overall texture of the ceramic body. The microtextural and petrographic analysis of the material is the starting point for all subsequent analyses (Kingery 1987, Middleton and Freestone 1991, Philpotts and Wilson 1994). The next step is to identify the mineral phases present as temper, as newly formed phases in the matrix, or as reaction phases at the matrix-grain boundary. The knowledge of the phases and of their crystal chemistry is essential to interpret the firing process on the basis of the mineral reactions and of the known phase diagrams (Heimann 1989, Riccardi *et al.* 1999). Most of the temper phases can be readily identified in thin section, but the newly formed