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Nuclear Techniques for Cultural Heritage Research

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INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2011

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Marketing and Sales Unit, Publishing Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
fax: +43 1 2600 29302
tel.: +43 1 2600 22417
email: sales.publications@iaea.org
http://www.iaea.org/books

Printed by the IAEA in Austria
September 2011
STI/PUB/1501

IAEA Library Cataloguing in Publication Data

Nuclear techniques for cultural heritage research. — Vienna : International Atomic Energy Agency, 2011.
p. ; 24 cm. — (IAEA radiation technology series, ISSN 2220–7341 ; no. 2)
STI/PUB/1501
ISBN 978–92–0–114510–9
Includes bibliographical references.

1. Nuclear technology — Archaeology. 2. Cultural property — Valuation. 3. Radiocarbon dating — Archaeology. I. International Atomic Energy Agency. II. Series.

IAEAL 11–00686

FOREWORD

Cultural heritage (‘national heritage’ or just ‘heritage’) is the legacy of physical artefacts and intangible attributes of a group or society that are inherited from past generations, maintained in the present and restored for the benefit of future generations. Physical or ‘tangible cultural heritage’ includes buildings and historical places, monuments, artefacts, etc., that are considered worthy of preservation for the future. These include preservation and conservation of objects significant to the archaeology, architecture, science or technology of a specific culture.

Scientific studies of art and archaeology present a necessary complement for cultural heritage conservation, preservation and investigation. As cultural heritage objects are frequently unique and non-replaceable, non-destructive techniques are mandatory and, hence, nuclear techniques have a high potential to be applied to study these valuable objects. Nuclear techniques, such as neutron activation analysis (NAA), X ray fluorescence (XRF) analysis or ion beam analysis (IBA), have a potential for non-destructive and reliable investigation of precious materials, such as ceramics, stone, metal or pigments from paintings. Such information can help to repair damaged objects adequately, distinguish fraudulent artefacts from real artefacts and assist archaeologists in the appropriate categorization of historical artefacts. Although the application of scientific methods to art and archaeological materials has a long tradition, it is due to the stimulation of institutions such as the United Nations Educational, Scientific and Cultural Organization (UNESCO), the United Nations Environment Programme (UNEP) and the IAEA that applications of natural science techniques are increasingly being accepted by museum curators and cultural heritage researchers.

The IAEA as a leading supporter of the peaceful use of nuclear technology assists laboratories in its Member States to apply and develop nuclear methods for cultural heritage research for the benefit of socioeconomic development in emerging economies. The IAEA had in the past initiated several projects to support the application of nuclear techniques to cultural heritage investigations and, as a result of a recently completed coordinated research project (CRP) entitled “Applications of Nuclear Analytical Techniques to Investigate the Authenticity of Art Objects” and building upon the expertise of dedicated experts, decided to compile a technical publication to highlight the role of nuclear techniques in cultural heritage research.

This publication provides information that helps to disseminate knowledge and encourage nuclear analytical researchers to liaise with art historians, archaeologists or curators of museums and make their analytical techniques available for the scientific investigation of art and archaeology where descriptive methods are limited. Following an introductory chapter, the second part of this book, prepared by dedicated experts in the field, describes particular fields of cultural heritage research and the third part provides an account of some of the participants' work during the CRP, demonstrating the successful application of the principles described in the first part. The attached CD contains the report of the CRP and participants' contributions.

The IAEA wishes to thank all contributors to this publication for their valuable contributions, especially M. Rossbach (Germany) for compiling and reviewing the book. In particular, the encouragement by J.L. Boutaine, the former Director of the Louvre Laboratories in France, has mediated further interest and encouragement to pursue this book project. The IAEA officer responsible for this publication was M. Haji-Saeid of the Division of Physical and Chemical Sciences.

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OVERVIEW

Chapter 1

INTRODUCTION

1.1. HISTORICAL DEVELOPMENT

The systematic application of scientific methods in the field of archaeology and art had its origin in the European research community and its first manifestation in the late eighteenth century with the published work by the German scientist Martin Heinrich Klaproth (1743–1817), who analysed the composition of some Greek and Roman metal coins.

The first museum laboratory dedicated to the study and conservation of cultural heritage was established by Friedrich Rathgen in 1888, when he was appointed head of a new scientific institution, the Chemical Laboratory of the Royal Museums of Berlin.

Throughout the first half of the twentieth century, new laboratories were established and they concentrated their efforts on answering analytical questions as well as those about the original materials and technology of the artefacts and monuments, settling the common basis of what can now be called ‘conservation science’. For example, the increased recognition of the importance of cultural heritage research was expressed by the delegates to the Eighth European Commission sponsored conference entitled “Cultural Heritage Research Meets Practice”, organized by the National and University Library and the University of Ljubljana, Slovenia, in November 2008 in the ‘Ljubljana declaration’. The importance of cultural heritage research was demonstrated by three facts:

(1) Cultural heritage is a non-renewable resource to be managed sustainably on behalf of present and future generations.
(2) Cultural heritage is key to the economic competitiveness of Europe with respect to tourism (with eight million workers and an annual turnover of €340 billion).
(3) The industrial market for European companies involved in conservation and restoration of cultural heritage is €5 billion per annum and is increasing.

These arguments apply equally well to other regions and are particularly important in developing countries where tourism represents a substantial economic resource.

At present, a strong cooperation between science and the arts is taking shape, mediated partly through guidance of international organizations such as the United Nations Educational, Scientific and Cultural Organization (UNESCO) and the International Council of Museums (ICOM). The IAEA, via their Coordinated Research and Technical Cooperation Programmes, is supporting Member State laboratories using nuclear and related technologies to collaborate with their colleagues from the art history, archaeological or museum branches, to take advantage of scientific investigations in cultural heritage objects. Among other fields, four major areas can be identified where scientific methods can contribute substantially to archaeological research:

(1) Conservation and/or restoration;
(2) Provenancing;
(3) Dating;
(4) Verification of authenticity.

General aspects, the principal methods applied and a few prominent examples of their use are described briefly in Sections 1.1–1.4.

It is important to note that the safety issues related to the use of radiation based techniques require compliance with national regulations.

1.2. CONSERVATION/RESTORATION

Conservation of artefacts has two phases:

(1) Preventive conservation, including cleaning and repair of artefacts and environmental controls in display and storage spaces;
(2) Conservation intervention, which is more treatment oriented and can be expensive.

Without conservation, however, most artefacts will perish, and important historical data will be lost. The loss is not just to the excavator but also to future archaeologists, who may wish to re-examine the material. When treatment is accorded to an object, it can include both conservation and restoration. Conservation refers to the process of documentation, analysis, cleaning and stabilization of an object. The main objectives of cleaning and stabilization are protection against, and prevention of, adverse reactions between the object and its environment. Restoration refers to the repair of damaged objects and the replacement of missing parts. A specimen may undergo both conservation and restoration but, in all cases, the former has priority over the latter.

It is important to continually stress that the proper conservation of artefacts is critical not only because it preserves the material remains of the past that are recovered but also because it is capable of providing almost as much archaeological data as do field excavations and archival research. This is possible if the problems of conservation are approached with an archaeologically oriented view of material culture. This view contributes sensitivity to the nature and potential value of the archaeological record and the importance of various types of association. An underlying premise of archaeology is that the distribution of cultural material, as well as its form, has cultural significance and is indicative of past cultural activities [1.1].

With regard to preservation of unearthed artefacts, there are a number of nuclear techniques to comply with the requirements outlined above. For insect eradication in wood or fungi and mould disinfection in, for example, mummies, paintings, books or tissue, ^{60}Co irradiation has been successfully applied [1.2]; for characterization of corrosion products on metallic artefacts X ray fluorescence (XRF) and X ray diffraction analysis are frequently used, X ray radiography is used if internal structures have to be investigated prior to treatment or to check the results of treatment [1.3]. Owing to their higher penetration capability, neutrons are also used for radiography of, for example, metallic artefacts to obtain an insight into their internal structure for possible conservation purposes [1.4, 1.5].

For preservation of easily deteriorating materials, such as wood from marine environments, polyethyleneglycol (PEG) impregnation followed by freeze drying or air drying has been used, for example, to preserve the Vasa, a sunken battleship from the sixteenth century in Sweden [1.6]. As an alternative, there is also in situ radiation curing through cross-linking of impregnated resin by irradiation with a strong ^{60}Co source, which seems to produce more stable protection of organic artefacts.

Restoring cultural heritage specimens, such as icons or paintings, that have deteriorated requires extended knowledge about the materials and processes the ancient artist was using. A whole suite of analytical techniques has been used to elaborate adequate procedures for restoration of paintings on canvas, wood or walls. Pigment analysis of frescoes can conveniently be obtained by in situ XRF analysis using portable instruments [1.7]. Scanning electron microscopy in combination with energy (or wavelength) dispersive microanalysis has been extensively applied to obtain information on the elemental composition of pigments and paint layers in tiny samples embedded in epoxy resin for cross-section analysis, in ancient glass or medieval silver coins [1.8]. Knowledge of the chemical composition of dyes can also help to identify fraud as production of paint has considerably changed over time. Some paintings have undergone several repair procedures during their lifetime adding non-authentic paint to the original. Art historians are keen to elaborate on these issues.

1.3. PROVENANCING

The stringent requirement to preserve the integrity of valuable cultural heritage objects being investigated called for methods with little or no sample consumption during the analytical process. Besides optical methods such as ultraviolet (UV) or infrared (IR) spectroscopy, nuclear based techniques became highly attractive for cultural heritage research after the dawn of nuclear research reactors. Hence, in 1956, J. Robert Oppenheimer, the Director of the Institute for Advanced Studies in Princeton, NJ, United States of America (USA), suggested "to apply the methods of nuclear research to the study of archaeology." R.W. Dodson and E.V. Sayre of the Brookhaven National Laboratory took up this suggestion and published their first paper entitled "Neutron activation study of Mediterranean potsherds" in 1957 [1.9]. With the advent of high resolution germanium detectors, this application received a lot of momentum and materials such as glass [1.10], obsidians [1.11] and coins [1.12] were analysed for elemental signatures to distinguish provenance or to determine precious metal content. Neutron activation analysis (NAA) has been recognized as the method of choice for archaeological provenance investigations since the 1970s [1.13].

As databases of archaeological materials began to develop, scientists from the Brookhaven National Laboratory were the first to apply a series of multivariate statistical procedures to studies of ceramics and other archaeological materials [1.14]. From this work the concept of the 'provenance postulate' was developed. The provenance postulate states that:

> "in order to trace artefacts to their source, or to group together artefacts from unknown sources, that there must exist differences in chemical composition between different natural sources that exceed the differences within a given source" (see Ref. [1.15]).

Thus, source determination efforts based on the provenance postulate require a comprehensive characterization of known sources of raw material or paste used in a pottery workshop to compare artefacts of unknown provenance with the range of variation of the known source groups [1.16]. If the sources are localized and relatively easy to identify, as in the case of volcanic obsidian flows, raw materials from the known sources are usually characterized and then artefacts of unknown provenance can be compared with the range of variation of the known source groups. Clay and pottery paste, turquoise and other gems, marble, basalt, ancient glass, copper and precious metals have been traced to their places of origin by using the fingerprinting method of trace elements determined by a suite of nuclear analytical techniques.

Prompt gamma activation analysis (PGAA) is a powerful method for non-destructive determination of major and trace element composition in a number of archaeological and other materials. Prompt and delayed gamma photons are detected following the (n, γ) nuclear reaction induced by neutrons from a research reactor or a neutron generator in semiconductor HPGe detectors. Gamma spectrum analysis allows quantification of the element composition of complex samples using either the standard comparison or the k_0 method [1.17]. A comprehensive description of the physical background, applications and a catalogue of all relevant prompt gamma lines is given in Ref. [1.18]. This technique is particularly sensitive for light isotopes (low Z) such as hydrogen (H) and boron (B), as well as cadmium (Cd), mercury (Hg) and rare earth elements, and also some bulk elements such as carbon (C), nitrogen (N) and sulphur (S) can be quantified. Provenancing of pottery and other archaeological materials has been successfully carried out using PGAA [1.19, 1.20].

A complementary method recently developed at the neutron spallation source at Rutherford Appleton Laboratories, United Kingdom (UK), is time-of-flight neutron diffraction (TOF-ND). Diffraction is a direct method for examination of the structural properties of a wide class of materials such as pottery, pigments, stone, marble and metal, providing information on phase composition, crystal and magnetic structure, microstrains and texture, i.e. whether or not grains have random or preferred orientation. The microstructure is generally related to the material properties and the fabrication process. Data treatment follows well established procedures such as quantitative Rietveld analysis for phase identification, lattice constant determination and quantitative assessment of the mineral composition, as well as texture analysis. Figures produced from texture analysis provide an elegant representation of disturbed grain orientation in a sample body due to, for example, casting, rolling, hammering or heating from the production process. If the historical manufacture techniques are known, texture maps may also help to distinguish genuine from fake artefacts [1.21–1.23].

1.4. DATING

An important objective in cultural heritage studies is to order past events chronologically by analysing materials associated with past human activities. Radiocarbon, or ^{14}C, dating is probably one of the most widely used and best known absolute dating methods. It was developed by J.R. Arnold and W.F. Libby in

1949, and has become an indispensable part of the archaeologist's toolkit ever since. In 1960, Libby was awarded the Nobel Prize in chemistry for this work. He first demonstrated the accuracy of radiocarbon dating by accurately measuring the age of wood from an ancient Egyptian royal barge whose age was known from historical documents. Its development revolutionized archaeology by providing a means of dating deposits independently of artefacts and local stratigraphic sequences. This allowed for the establishment of worldwide chronologies.

Carbon has two stable non-radioactive isotopes: ^{12}C and ^{13}C. In addition, there are trace amounts of the unstable isotope ^{14}C on earth, which is created in the atmosphere by cosmic ray impact on ^{14}N:

$$n + {}^{14}_{7}\mathrm{N} \rightarrow {}^{14}_{6}\mathrm{C} + p$$

Carbon-14 has a half-life of 5730 ± 40 years, meaning that the amount of ^{14}C in a sample is halved over the course of 5730 years due to radioactive decay.

Plants take up atmospheric carbon dioxide by photosynthesis, and are ingested by animals, so that every living organism is constantly exchanging ^{14}C with its environment as long as it lives. Once it dies, however, this exchange stops, and the amount of ^{14}C gradually decreases. Measurements of ^{14}C are traditionally made by counting the radioactive decay of individual carbon atoms by gas proportional counting or by liquid scintillation counting. For samples of sufficient size (several grams of carbon), this method is still widely used at present. The sensitivity of the method has been greatly increased by the use of accelerator mass spectrometry (AMS). With this technique, ^{14}C atoms can be detected and counted directly and not just by detecting those atoms that decay during the time interval allotted for an analysis. Accelerator mass spectrometry allows dating of samples containing only a few milligrams of carbon.

Since the atoms and not the radiation resulting from their decay are directly counted, the sensitivity of AMS is unaffected by the half-life of the isotope being measured and detection limits at the level of 10^6 atoms are possible. Compared with the decay counting technique, the efficiency of AMS in detecting long lived radionuclides is 10^5–10^9 times higher, the size of the sample required for analysis can be 10^3–10^6 times smaller and the measurement can be performed 100 to 1000 times faster. Van de Graaff tandem electrostatic accelerators are the optimum choice for a variety of AMS applications. Tandem accelerators working between 0.5 and 3 MV have been specifically designed for ^{14}C analysis.

Originally assumed to be an absolute dating technique, the perspective slightly changed when some of the fundamental assumptions of the Libby method proved to be invalid. The construction of the 'radiocarbon dating calibration curve' from meticulously counted annual tree ring segments showed that the exchangeable carbon reservoir is variable over time and, hence, the ^{14}C dating method was valid only within the errors of the validation measurements [1.24]. However, using modern techniques and the most sophisticated correction algorithms currently available, it is possible to achieve a high level of accuracy and precision of around 0.2% using AMS with only a few milligrams of carbonaceous samples. Some of the most spectacular applications of AMS dating of cultural heritage materials include the investigation of the Shroud of Turin [1.25], the Qumran papyrus manuscripts [1.26] and the ageing of the iceman [1.27] from the Ötztal, Italy.

Another important dating technique for archaeologists is luminescence dating, either as the thermostimulated or optically stimulated version, depending on the radiation used to release trapped electrons in quartz and feldspar grains. The essential basis of dating pottery is that the firing of the raw clay sets to zero the latent signal being build up during burial due to the weak flux of alpha (^4He), beta (e^-) and gamma rays from thorium (Th), uranium (U) and potassium (^{40}K), with a minor contribution from cosmic rays in addition. The radioelements are present in the clay itself and in the burial soil. The annual dose from these is determined either by radioactive analysis or by more direct methods (e.g. inductively coupled plasma mass spectroscopy (ICP-MS)). Laboratory measurement of the sample's 'natural' themoluminesence and of its sensitivity to acquisition of thermoluminescence due to exposure to the flux from a radioisotope source allows evaluation of the 'paleodose' — the accumulated dose that the sample has received since firing in antiquity [1.28]. This method proved to be also valid beyond the timeframe of the ^{14}C method and can be extended up to 100 000–500 000 years. A comprehensive guideline for using thermoluminescence dating in archaeometry is given in Ref. [1.29].

1.5. AUTHENTICITY VERIFICATION

Forgery of cultural heritage objects is a widespread problem that affects particularly the trade in artefacts and has a considerable economic impact. As imitations can be produced to resemble the original appearance perfectly well, scientific investigations to study composition or age are the only definitive tools to clarify the authenticity of materials. Virtually all methods described above have the potential to assist in these investigations; additionally, ion beam analysis (IBA) techniques can be of substantial help [1.30], particularly in the in-air version [1.31]. This development, including particle induced X ray emission (PIXE), particle induced gamma ray emission (PIGE) and Rutherford backscattering (RBS) by use of appropriate detector systems, allows elemental information to be obtained from large objects without any impact on the integrity of the precious materials. Although it is only a surface analytical approach, some depth information can be collected by adjusting the proton beam energy. Large accelerators devoted to the investigation of cultural heritage and art objects are operational in a few national museums and research establishments, such as the AGLAE facility at the Louvre Museum in Paris, France, the LABEC facility at INFN, Florence, Italy, [1.32] or the IBA facility at the Forschungszentrum Dresden, Germany. A detailed survey of available accelerator based analytical techniques was compiled by the IAEA in 2005 [1.33].

Isotopic techniques based on mass spectroscopic principles are most suitable for authenticity verification. The U, Th–^{4}He method has been recently successfully demonstrated in the verification of the authenticity of gold artefacts [1.34]. This technique relies on a precise and sensitive mass spectrometric determination of the trapped alpha particles from U and Th decay. These alpha particles are released when metal is molten and accumulate as long as the artefact did not undergo any melting process. Along with spectrometric determination of U and Th, the ^{4}He content of tiny amounts of gold (≈20 mg) can specify the age of a piece of jewellery.

The subject of authentication of cultural heritage is very delicate in principle and follows the lines of forensic science. It is connected not only to the economic value of a piece of art but also to the aesthetic, cultural and scientific significance of that piece. It is believed that even in well known museums, as well as in many private collections, non-identified fakes are widespread and techniques for their reliable identification have still to be developed [1.35]. Nuclear based techniques can substantially contribute to this important task when their inherent advantages are exploited.

1.6. SCOPE OF THE BOOK

This IAEA publication was initiated following a coordinated research project (CRP) entitled “Application of Nuclear Analytical Techniques to Investigate the Authenticity of Art Objects”, with 16 laboratories participating, and is a guide for other interested researchers summarizing the expertise and practical experience of the participants to this CRP. The intention is to provide a broad range of information (with ample references for those who wish to go deeper), selected interesting examples and applications to stimulate researchers from both sides, the natural sciences as well as the humanities, to merge their interests so that they can benefit from each others’ experience. The close cooperation between these communities can lead to exciting new projects and valuable insights into patterns and processes contributing to our present perception of cultural heritage. As the number of techniques, as well as their applications and the materials being investigated, is exceedingly large this book can only shed light on a few selected examples, but it includes some of the most prominent ones.

Part II of this publication describes the scientific methods, in particular, fields of cultural heritage research, such as the conservation/restoration of paintings (Chapter 2), the use of analytical data for provenancing of pottery (Chapter 3), dating of (metallic) artefacts (Chapter 4), authenticity verification of jewellery (Chapter 5), and a special development of nuclear techniques for non-invasive tomography and analysis of compact artefacts (Chapter 6). Part III gives an account of some of the participants' work presented during the CRP, demonstrating the successful application of the methods described in Part II. This is just a selection of the reports generated; the unedited reports of the CRP as presented at the final research coordination meeting are included as support material with this book on the attached CD-ROM.

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Part II

THE SCIENTIFIC METHODS USED IN CULTURAL HERITAGE RESEARCH

Chapter 2

CONSERVATION OF PAINTINGS

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2.1. INTRODUCTION

Ever since Martin Heinrich Klaproth (1743–1817) performed a chemical analysis of the terracotta from Tiberius's villa on the island of Capri for the first time at the end of the eighteenth century, more and more sensitive and mutually complementary physicochemical methods are being developed to study works of art and archaeological artefacts. Technological studies, studies of manufacturing techniques, of the appearance of ageing and methods for determining the age of objects are performed, firstly, to determine the authenticity of works of art, secondly, to obtain information on the technology and techniques that were used by a given master, and, thirdly, to indicate the optimum conservation techniques that should be used during renovation and conservation work of a given object.

On the one hand, archaeometry and research on works of art and, on the other hand, the protection of works of art and historical objects constitute the two main areas of these somewhat unique studies, especially material studies. The first area concerns mainly cognitive goals, for instance, determining the authenticity of an object or identifying forgeries, determining the origin of the object and its dating, and discovering the technology used for making such products. The second area relates to applied studies: it accumulates research that is aimed at developing methods for the protection of historical artefacts in the broader meaning of the term.

In both cases, we endeavour to achieve our goals by determining the object's technological construction, identifying the materials used in its production, reconstructing the technological processes used for manufacturing the object, assessing its condition, determining the reasons why and how the object was damaged, reconstructing its original form, etc.

The specific feature of such research is the use of multiple methods, mainly physicochemical, to study objects of a unique nature, of a high artistic value and a high market value. Often it is impossible to collect material, or even a small analytical sample, for testing. In such instances, portable equipment and various methods which are not damaging to the object and do not require sampling are used. The terms ‘destructive’ and ‘non-destructive’ must be understood — in this context — as relating to the whole work of art, and not only to the analytical sample taken. Taking an analytical sample could, for instance, lead to a risk to the historical object, could disfigure it or reduce its artistic or market value.

The objects themselves are often very heterogeneous. This is due, among other reasons, to the composite materials they are made of, their complex technological construction and natural ageing processes. Their external layers, to which we usually have unrestricted access, and which we see when viewing an object, do not fully represent the material from which the object was initially manufactured. In addition, the chemical components of the external layer often differ significantly from the chemical composition of the material from which the object was produced. This leads to serious problems concerning interpretation, and taking samples from the deeper, non-corroded, layers could lead to even greater damage to the object. However, taking samples is necessary for the performance of many tests. Therefore, the size of a sample, which in this case is understood more as a potential visible detriment to the object than as a minimum necessary weight, is of importance. The issue of the sample size is currently a real challenge for researchers engaged in studies of works of art [2.1, 2.2].

The selection of the research method used must each time be well thought out, taking into consideration mainly the purpose of the test and the nature of the tested object. For a long time now, nuclear techniques have been considered to be one of the most important research techniques for identifying works of art, due to their great sensitivity and the possibility of discovering features that are invisible to the naked eye. These methods can generally be divided into three categories:

(i) The first category covers various radiography techniques such as X ray radiography, xeroradiography, computed tomography, thermal neutron induced autoradiography, X ray induced autoelectronography, gamma radiography and neutronography. These make it possible to obtain information on the internal construction of an object, they do not require that samples be collected from the object and, in this sense, are non-destructive methods. The information obtained from this type of research often comprises basic information on the object which may be expanded and supplemented using other methods.

(ii) The second category includes all the analytical techniques using nuclear techniques which allow microelements to be traced in the tested objects. This enables the source of the object to be identified by observing similarities in the chemical composition, based on the assumption that the same types of materials which come from different sources should differ in terms of the content of microelements. The so-called fingerprint of the elements in a given object depends not only on the location where the material was collected but also on the technological process used in its production. Two main methods are used for this purpose: neutron activation analysis (NAA) and X ray fluorescence analysis. Another method for assessment of the source of origin of the materials is an analysis of the isotopic ratio of stable isotopes.

(iii) The third category includes techniques which use ionizing radiation directly in conservation work: radiation disinfection and radiation consolidation.

Radiation disinfection consists of using ionizing radiation to destroy bacteria, moulds, fungi and insects found in the objects. Radiation consolidation uses ionizing radiation energy to harden a liquid component with which the object under conservation is saturated. This treatment consolidates the structure of the object and preserves it from further destruction [2.3–2.6].

2.2. PAINTING, TESTING AND CONSERVATION

Paintings are an important part of our cultural heritage and have always exerted a fascination. The interest in them was accompanied by the development of historical research, the emergence of cultural history as an independent discipline, consolidating the concept of museology, making collections available and publicly accessible, and the beginnings of what we now call ‘conservation science’. The number of published monographs, research papers, articles and dissertations on conservation, restoration and scientific problems related to the analysis and protection of paintings attest to the significance of this area of our cultural heritage. If we also take into consideration research on the pigments which were used both in painting and in other works of art, such as polychrome sculptures, ceramics, frescoes, murals, furniture, jewellery and illumination of manuscripts or cosmetics, the number of works published is more than 60% of all publications that are thematically related to cultural heritage. This chapter presents only a small number of the problems related to the conservation of and research on oil paintings.

In the history of painting, the evolution of painting techniques, from the use of tempera, through oils, to oil and resin paintings and mixed techniques, is particularly interesting.

A painting is a complex multidimensional structure in which each element is subject to inevitable changes and reacts differently to external factors. These changes which occur independently result in the ageing of paintings, hence acquiring a new value which transforms constantly and irreversibly. After four hundred, three hundred, two hundred or even less than one hundred years have elapsed, a painting is also partly the creation of time and history. When looking at the arrangement of the painting layers on a small paint sample taken from a painting, we see how the painter achieved the colour and texture of particular areas of colour, we can see the optical changes that have taken place in the pigments and binding media, and the new layers of paint applied by the restorers. A sample of only a millimetre in size, usually referred to as a cross-section, is actually a cross-section of the painting's history [2.7].

Changes in humidity and temperature have warped the panel supports and distorted the surface of the canvas, as a result of which the paint, which is not flexible and did not succumb to the movements of the support, has become insecure in many places and fallen away from the painting. Many colours have changed their hues and the paint has become transparent due to chemical changes which occurred between the various components: dyes, pigments and bonding media. Artistic effects which were not anticipated by the artists arose; in many paintings the dark ground or the underdrawing of the composition on a white ground becomes visible. The surfaces of paintings have cracked, forming craquelures which vary in type and size, the varnish has blackened and dirt has become ingrained in the surface.

For many decades, attempts were made to prevent or liquidate the effects of these changes, usually ineffectively; moreover, methods were used which led to further damage. Even cleaning the paintings and replacing the matt appearance and darkened varnish led to unwarranted interference with the original paint layers, because the chemicals used were too drastic and the effects of the treatment became irreparable. Although the paintings were damaged, they had to fulfil their religious or decorative functions. So they were returned, after being unsuccessfully overpainted, including layers of new paint which were intended to hide the effects of the natural ageing processes of the painting materials or an incompetent restoration [2.8–2.10].

Often old and sometimes even modern renovation work was conducted without any real understanding of the painting's construction or how the artistic effect was achieved. Many of the materials used for conservation work, even for purely technical interventions, such as impregnation or affixing the relining, led to optical changes in the paintings concerned.

The results of technological and material studies, confronted with knowledge of particular artistic techniques, help us to attribute the paintings, date them and reconstruct their history. Reconstructing the fate of the pictures and their historical restorations also contributes to enriching our knowledge of changes in the aesthetic tastes during particular epochs and to the creation of modern conservation ethics and methodologies. The development of technological studies and more exhaustive research into archives may help explain the at present unknown stages of the history of a painting and subsequent restoration work. They enable researchers to more comprehensively attribute the studied paintings to the oeuvre of particular masters, especially when stylistic and technological comparisons are not falsified due to secondary, often very extensive, retouching and overpainting.

Currently, the aim of conservation work is to remove — as far as is possible — accumulated paint layers resulting from previous conservation and restoration work on paintings, protect the original subject matter of the work and integrate the work, in accordance with the particular style, technological construction and condition of the object. Very often paintings have been extensively retouched in the form of overpainting, which often covered the preserved original paint layers. Retouching is often an eighteenth and nineteenth century aesthetic interference which was not always due to the poor condition of the paint layers, but was also the result of changes in artistic tastes. These alterations were not only the result of overpainting but also of changes to the composition which necessitated making the support larger (by adding strips of canvas or strips of wood). The latter also interferes with the proper reception of paintings: alterations made to retouching, inconsistent thickness, often very thick, blackened and often coloured with a secondary varnish. Sometimes intentionally preserving the overpainting is acceptable if it is justified by the exceptionally poor condition of the original paint layers, and if the paintings are of an artistic and historical value. The basic assumption in the conservation work at present is to show the paintings in the form that most faithfully represents the original intentions of the artists without concealing the natural ageing process of the paintings [2.11].

2.2.1. Technological studies of paintings

Until the mid-1950s, technological studies were usually conducted to support conservation work. They were usually limited to basic diagnoses, i.e. an analysis of the luminescence of the painting's surface induced by UV radiation and a basic chemical analysis of the pigments. Occasionally, X rays or infrared reflectography (IRR) were used or detailed dendrochronological examinations and tests of the textile structure have been carried out. Attempts at more in-depth and detailed physicochemical studies were only made sporadically.

When undertaking any studies of easel paintings or polychrome sculptures, their complex structure should be taken into consideration. In the case of paintings, only one coat or several coats of size is/are used on wooden, canvas or metal supports (Fig. 2.1). An underdrawing can be executed, followed by a coat that reduces the absorptivity of the paint by the size. The bottom layer of paint is usually called the ground for the external paint layer, which has a transparent coloured layer called the glaze. The final layer that protects the paint from contamination and UV rays, and which deepens the colours, is the varnish. Retouches of the varnished layer are possible. This system of layers was used by

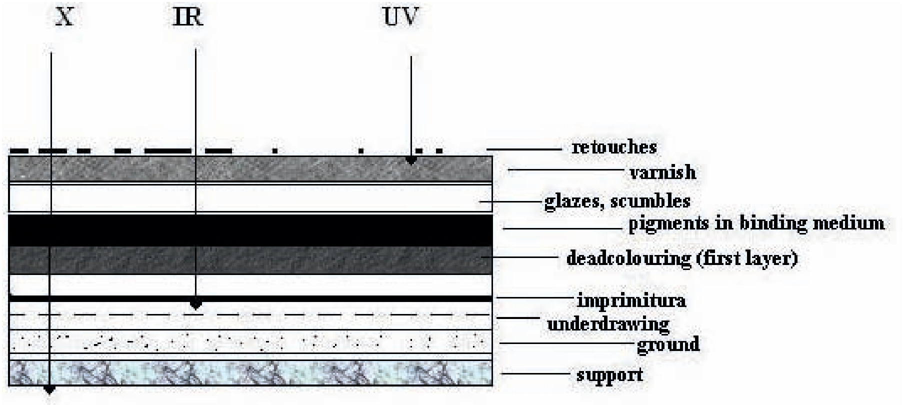

FIG. 2.1. Structure of paint layers and depth of penetration of electromagnetic radiation with different wavelengths.

artists from the Middle Ages up to the nineteenth century. It was expanded or simplified depending on the period in the history of painting, the school of painting or the preferences of individual artists.

However, it does not cover instances when an old painting constituted a support for a totally different, new, composition which introduced new layers.

During the first stage of research on a painting, basic studies are conducted using UV, IR and X rays, analyses of the paint layers based on stratigraphy and initial identification of pigments. Comparative analysis of the results from all studies, together with information on the treatment of the painting, enables the appropriate conservation measures to be taken.

A physicochemical analysis of a painting is aimed at determining the exact nature of the various materials and the technical features of paint application (used in the construction of the consecutive layers), stating their condition. The results of the research are important for both the art conservator and the historian. For the latter, recognizing the individual characteristics of the artist which are invisible to the naked eye on the picture, i.e. the nature of the lines of the invisible sketch, the strokes and dabs of the brush, the compositional changes made in the process of creating the painting, etc., is of special importance. Most of the information pertaining to the spatial nature of the different layers of the painting that is invisible to the naked eye is usually obtained from studies which use different parts of the electromagnetic spectrum. These methods — which have been in use for more than fifty years — are being constantly enhanced; they do, however, have many limitations. Thus, photoluminescence induced by UV rays only shows changes on the surface of the painting: retouching, overpainting, the condition of the varnish, etc.

Infrared rays with a wavelength of up to about 2 μm penetrate the surface of the painting to find the 'earlier underdrawings' under the layers of paint, provided it was executed in black on a white binding medium.

X rays penetrate the whole painting, but the X ray photograph only shows the layers including elements with a high atomic number. It is possible to see the manner in which the paint was applied, which typifies an individual artist's work, if pigments such as lead-tin yellow, cinnabar and white lead have been used.

In the event that white lead is found in the binding material or in the pentimenti[1], which is frequently the case, X rays do not provide any information about the thin layers (thick layers absorb more X rays than thin layers). Although the influence of highly absorbent ground and lower layers of the painting may be reduced by making autoelectronograms induced with high energy X rays, they only show the distribution of substances with a high atomic number. New research possibilities were discovered with the use of neutron induced autoradiography.

Further detailed studies of paintings are aimed at identifying the painting materials and techniques used during the creation process of the painting and during any past renovations. An important element of this stage of research is a close observation of the painting during the removal of the varnish, retouching, overpainting and cleaning the original support of the painting [2.12–2.15].

An analysis of the pigments used in paintings is of the utmost importance in order to develop appropriate methods for their conservation, as it provides the detailed characteristics of the materials and enables their origins to be determined. Individual features that typify a specific artist can also be extracted. Study of pigments is a very difficult science. Firstly, the diversity of the pigments used is vast — about 500 non-organic pigments have been identified in the history of art. Secondly, each element of a painting undergoes unavoidable changes and reactions to external factors, the effects of which are irreversible. Thirdly, each painting is a unique work of art and often no analogies can be found. As a consequence, it is not possible to use the various routine research methods applied to other areas of science; they have to be adapted, or the measuring equipment has to be adapted to the specific purposes required. Such research must be conducted on the basis of assumptions and procedures determined each time with reference to the given historical object.

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[1] A **pentimento** (plural **pentimenti**) is an alteration in a painting, evidenced by traces of previous work, showing that the artist has changed their mind as to the composition during the process of painting. The word derives from the Italian *pentirsi*, meaning to repent.

Research on pigments has been conducted for many years in various research centres. Databases are being created, and manuals and encyclopaedias have been published [2.16–2.19]. Several analytical methods are used, such as:

(a) Scanning electron microscopy with X ray microanalysis (SEM-EDX), electron probe microanalysis (EPMA), secondary ion mass spectrometry (SIMS), X ray powder diffraction (XRD), NAA, XRF, total reflection X ray fluorescence analysis (TXRF), micro-Fourier transform interferometry (μ-FTIR), gas chromatography mass spectrometry, thermal microscopy, PIXE, PIGE, Mössbauer spectroscopy, Fourier transform spectroscopy, inductively coupled plasma mass spectrometry (ICP-MS) and gas chromatography mass spectrometry (GC-MS) — to identify organic substances (varnishes, mediums and organic pigments);
(b) Neutron autoradiography — to determine the arrangement of the pigments and infills used, and microchemical methods and microscopic methods (microcrystallography, microtexture analysis, petrographic analysis and mineral analysis) [2.20–2.35].

The greatest problems occurring in studies on materials found in works of art concern the identification of organic substances. In the case of easel paintings, the binding media, varnishes and pigments used in the glazing constitute complex mixtures of organic substances. As the paintings become older the complexity of the mixtures builds up as a result of oxidation, polymerization, etc. Conservation work also introduces new organic substances into paintings. The type of binding media used may depend on the pigment used and may vary in different parts of the painting. There is an additional difficulty that exacerbates an already complex analytical problem: this relates to the amount of the sample that may be taken from the paint layers or the remains of the glazing. One of the methods used for studying organic substances is infrared spectrophotometry. The limitations of this method, related to the low resolution capacity and the need to collect large samples for analysis, are to a large extent offset by using μ-FTIR. Another modern analytical method is GC-MS, which is particularly useful in research on organic mixtures. Only by using both methods is it possible to obtain satisfactory results from microscopic samples [2.36–2.38].

All these methods are sensitive, mutually complementary, physicochemical methods and enable information to be obtained from the microsamples collected (about 0.3 mg) or by using non-invasive methods.

Determining the techniques used to create the painting — discovering the sequence and method of applying particular layers of paint — is of significant importance when determining the authenticity and attribution of a painting. As a matter of fact, at any given time, the same painting materials could have been used by various artists and only an analysis of the working method used in the painting can lead to identification of the original artist.

2.2.2. Neutron induced autoradiography of paintings

Since the mid-1960s in the USA [2.39–2.41], the end of the 1980s in Germany [2.42–2.46] and 1997 in Poland [2.47–2.49], thermal neutrons, which induce moderate but temporary radioactivity, have been used to analyse the internal structure of paintings. The procedure of this method is as follows: after taking the painting out of its frame, it is evenly irradiated with thermal neutrons in the guided beam of a nuclear research reactor. After 'activation', an X ray film attached tightly to the surface of the painting (through the application of slight vacuous pressure) is exposed to the radioactivity formed in the painting to locate the dispersion of radioisotopes and assess the concentration of elements with different half-lifes.

These reflections on the film are known as autoradiograms and are usually the effect of beta radiation. Initially, autoradiograms register short lived isotopes such as ^{56}Mn (2.6 h), ^{38}Cl (37 min) or ^{47}Ca (4.5 d), and on consecutive films, which are exposed for longer and longer periods, radioisotopes are disclosed with average and longer half-lives such as ^{59}Fe (44.5 d), ^{203}Hg (46.6 d) or ^{110m}Ag (246 d). In this manner, a series of autoradiograms can be obtained which differ among themselves on which specific radioisotopes are discerned. In order to produce a distinct photographic image for long lived radioisotopes within a reasonable timeframe, the picture has to be exposed to a thermal neutron fluence of 10^{11}–10^{13} n/cm^2. The time of contact of the irradiated picture with the X ray film for consecutive autoradiograms is more or less equal to the amount of time that passed from the end of the radiation process in the reactor to the time of starting the exposure of the film, and more specifically it is determined by measuring the radiation intensity emitted by the painting. Gamma ray spectrometry plays an important role in this method. The overview of the gamma radiation spectrum of the whole painting and the measurements made on different coloured areas between consecutive exposures of autoradiograms enable the radioisotopes to be determined and resolve which of the two isotopes with similar half-lives contributed to the blackening of the film. Apart from quality analysis, spectrometric measurements assess the content of the radioisotope more accurately than the blackening of the film, resulting from the layers of various thicknesses. The major isotopes found in old paintings, along with their half-lives as well as the names of the pigments in which they are present, are specified in Table 2.1.

TABLE 2.1. CHEMICAL ELEMENTS AND RADIONUCLIDES IN THE MOST CHARACTERISTIC PIGMENTS

Element	Pigment	Radionuclide (n, γ)	$T_{1/2}$ (half-life)	$E_{av,\beta}$ (average beta energy)
Manganese	Umber, dark ocher	Mn-56	2.6 h	1.84 MeV
Copper	Malachite, azurite	Cu-64	12.8 h	0.57 MeV
Potassium	Smalt, glue	K-42	12.5 h	3.27 MeV
Sodium	Glue, medium canvas, ultramarine	Na-24	15 h	1.39 MeV
Arsenic	Smalt, realgar, auripigment	As-76	26.5 h	2.55 MeV
Antimony	Naples yellow	Sb-122 Sb-124	2.8 d 60 d	1.5 MeV 1.02 MeV
Mercury	Vermilion	Hg-203	47 d	0.21 MeV
Cobalt	Smalt, glass	Co-60	5.26 a	0.31 MeV

Autoradiograms, representing the entire pictures, disclose the internal structure of a painting and supplement the frequently limited content of X rays with additional information, disclosing details which before could not be discovered using other methods. For example, seventeenth century Dutch painters added ground glass to black paints to give them their characteristic luminescence. This is confirmed by the arsenic discovered in amounts that are typical for glass, and present on the autoradiograms in places reflecting the black and dark parts on the paintings. On the other hand, many elements present in paintings are not found in autoradiograms. These include lead, phosphorus and organic compounds. The isotope ^{59}Fe, which can be found in many pigments, on almost any painting, owing to its small cross-section for the (n, γ) reaction, only contributes to a small extent to blackening autoradiograms. For this reason, the results of neutron induced autoradiography must also be supplemented by specific additional studies.

In 1997, a station for neutron induced autoradiography of paintings was constructed at the MARIA research reactor in Swierk near Warsaw, Poland [2.7, 2.47–2.49].

Several paintings by Venetian masters from the National Museum in Warsaw were selected for the neutron autoradiography method, based on analysis of their X ray radiographs. Figure 2.2 represents ‘Portrait of a Venetian Admiral’ by

FIG. 2.2. 'Portrait of a Venetian Admiral' by Tintoretto.

Tintoretto (1518–1595) (oil on canvas; 81 cm × 68 cm) in visible light. The ultraviolet examination is shown in Fig. 2.3. The darker areas are those which were covered by the frame. The irregular black spots of different intensities are the retouchings that were made at various times. The infrared reflectogram (Fig. 2.4) and X ray image (Fig. 2.5) reveal a hidden portrait of a man in a different garment compared with the admiral with a headgear. The face of the admiral and the collar visible on the infrared reflectogram are from an earlier likeness.

Initial analyses (X ray analysis and stratigraphic analysis of painted layers) regarded the portrait as an advanced composition with adjustments made by the artist later: the original large flat collar was made smaller. The drapery brocade pattern served as the background. However, the observations made during conservation work, which involved removing varnish and extensive inpaintings, led to the conclusion that the previous portrait could have been more advanced in terms of presenting the face and the collar while the bust was only contoured with thick brush strokes of white paint. These observations were confirmed by neutron induced autoradiography experiments. Figure 2.6 shows the first autoradiograph

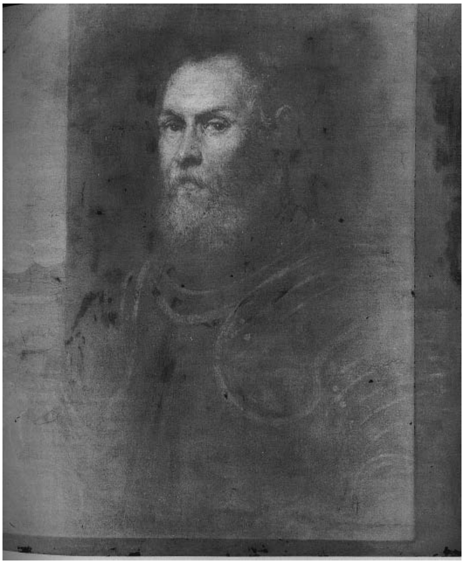


FIG. 2.3. An ultraviolet image of the painting shown in Fig. 2.2.

FIG. 2.4. An infrared reflectogram of the painting shown in Fig. 2.2.

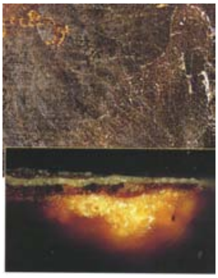
of the portrait. The autoradiograph shows facial features and the discontinued stage of the hidden painting. The blackening of the X ray film originated in the places where umber was applied as a result of manganese radiation detection (^{56}Mn); however, it is the mercury radiation (^{203}Hg), present in vermilion and

FIG. 2.5. An X ray image of the painting shown in Fig. 2.2.

FIG. 2.6. The first autoradiograph, with an exposure time of three hours, of the painting shown in Fig. 2.2.

copper (^{64}Cu) in copper blue and green pigments, that is responsible for the blackening visible in autoradiograph No. 3, shown in Fig. 2.7.

FIG. 2.7. The third autoradiograph, with an exposure time of 32 hours, of the painting shown in Fig. 2.2.



Scheme of painting layers. Mag. 125x

1. bright layer – ground: gypsum, basanite
2. brown layer - ground: mixture of pigments – umber, lead white, lead-tin yellow, vermilion, copper pigment, haematite
3. thick white layer – the first collar: lead white, marble

FIG. 2.8. Fragment of the admiral's beard. Photomicrograph of the cross-section of the paint in the Tintoretto painting shown in Fig. 2.2.

The cross-section of the paint layer in Fig. 2.8 (the method of grinding the paint, the presence of coarse mineral filler in all layers) and analysis of pigments revealed also that the two overpainted portraits come from the same workshop [2.7].

Another painting studied with the use of the neutron autoradiography method was the painting by M. Marieschi (1710–1744), (oil on canvas; 41 cm × 52 cm) entitled 'The Palace of Doges in Venice' (Fig. 2.9). The reproduction of autoradiograph No. 4 (Fig. 2.10) shows a blackened strip of a painting planned before (^{124}Sb antimony detection), as well outlined figures,

FIG. 2.9. 'The Palace of Doges in Venice' by M. Marieschi (1710–1744).

FIG. 2.10. The fourth autoradiograph, with an exposure time of 14 days, of the painting shown in Fig. 2.9.

boats and architectural elements painted with the use of vermilion (^{203}Hg) and Naples yellow (^{124}Sb). We can only guess what the shape of the original composition would be; the image is visible on the autoradiograph (it should be turned by 90º compared with the present composition), where the film's darkening shows the underpainting of water, with a gondola and the contours of the waterside [2.7].

The largest painting that was irradiated in the nuclear reactor is a painting by B. Bellotto (1720–1780), 'Fantasy architecture with self-portrait of the artist' (oil on canvas; 154 cm × 112 cm), shown in Fig. 2.11. In Fig. 2.12, the X ray image and, in Fig. 2.13, the first autoradiograph of that presentation are shown. The ancillary lines made by the author in the process of preparing the composition of the painting are reflected by ^{56}Mn detection. In autoradiograph No. 4 (Fig. 2.14), there are black areas corresponding to the distribution of Naples yellow (^{124}Sb detection), i.e. a scarf of the artist, and vermilion (^{203}Hg) used to reflect the complexion and red garment of the figure.

Currently, new methods of imaging are being developed which use different types of ionizing radiation, such as confocal X ray microscopy, multispectral illumination methods, thermographic techniques, scanning acoustic imaging, air coupled ultrasound, Raman spectroscopy and imaging, non-destructive synchrotron X ray diffraction, synchrotron based K edge imaging and others [2.50–2.58]. The neutron autoradiography method continues to reveal a huge potential for studies of paintings; the basic drawback is the high cost of research and the need to have a nuclear reactor for research purposes.

2.2.3. Provenance of artistic materials

For the art historian, knowledge of the origin of the materials incorporated in works of art, specifically in specimens of anonymous works, is important. This can be discovered by measuring the concentration of trace elements and the isotope ratios in the artistic material and in the respective supposed source material. From the analyses conducted, it transpires that the isotope ratios in lead which come from lead white used by artists before 1800, and specifically those that are found in paintings of Dutch, Flemish and Belgian masters, are limited [2.59–2.61]. On the basis of quantitative analyses to date of trace elements in lead white collected from paintings dating from the fifteenth to the nineteenth centuries, it can be concluded that lead white originating from regions south of the Alps, found inter alia in Venetian paintings, shows a higher content of copper and manganese and a lower content of silver and antimony compared with lead white from regions north of the Alps, mainly applied in Northern Europe [2.62, 2.63].

FIG. 2.11. ‘Fantasy architecture with self-portrait of the artist’ by B. Bellotto (Canaletto) (1720–1780).

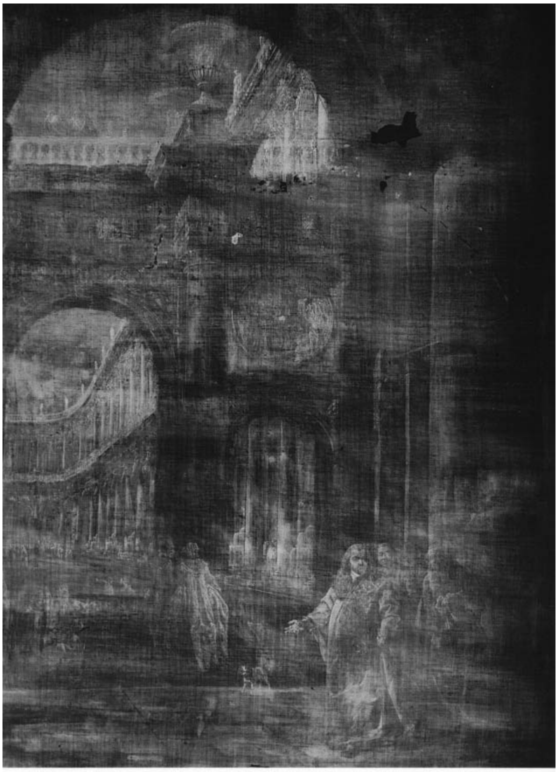


FIG. 2.12. An X ray image of the painting shown in Fig. 2.11.

The isotope ratios of sulphur from natural ultramarine definitely differentiate the sources of its origin. In respect of lapis lazuli from Afghanistan, the sole source of the blue pigment for all European painters until the first half of the nineteenth century, the measurement results do not reflect any other, later, sources of the mineral [2.64]. The attempts to measure isotope ratios for other elements, for example, for carbon ($^{12}C/^{13}C$), are not representative enough to draw any conclusions to date.

2.2.4. The ^{14}C and ^{210}Pb methods

The conventional ^{14}C method used for dating cannot be applied to 300–400 year old paintings or sculptures. Moreover, in the years 1950–1960 the amount of ^{14}C in the atmosphere nearly doubled due to above ground nuclear bomb testing. This type of change was reflected in plant products such as linseed oil, which is usually produced several months after harvesting and is rarely stored

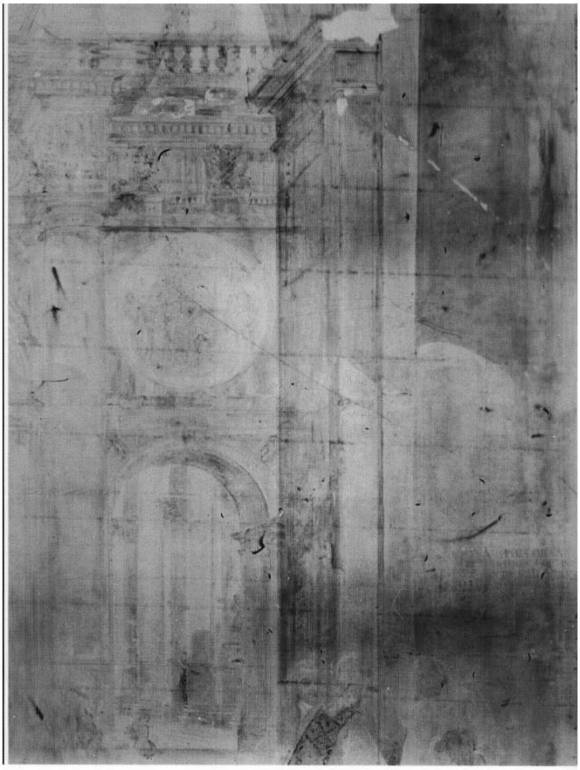


FIG. 2.13. The first autoradiograph, with an exposure of three hours, of the painting shown in Fig. 2.11.

for long periods. The paper by B. Keish and H.H. Miller [2.65] fully confirms the high content of ^{14}C in oils produced since the beginning of the 1960s. This may be used to disclose falsified or forged works of art, which were allegedly executed before 1950. In addition, the measurement of the content of ^{210}Pb in lead white may be used to discover contemporary falsifications. If the radioactive isotope ^{210}Pb is disclosed in a much higher content than its long lived precursor ^{226}Ra, it could mean that a painting is less than 200 years old (around ten times as long as the half-life of ^{210}Pb). If there is no amount of detectable ^{210}Pb, it can be deduced that the picture is rather old or that the lead white was prepared using an ore that did not contain radiogenic lead [2.66].

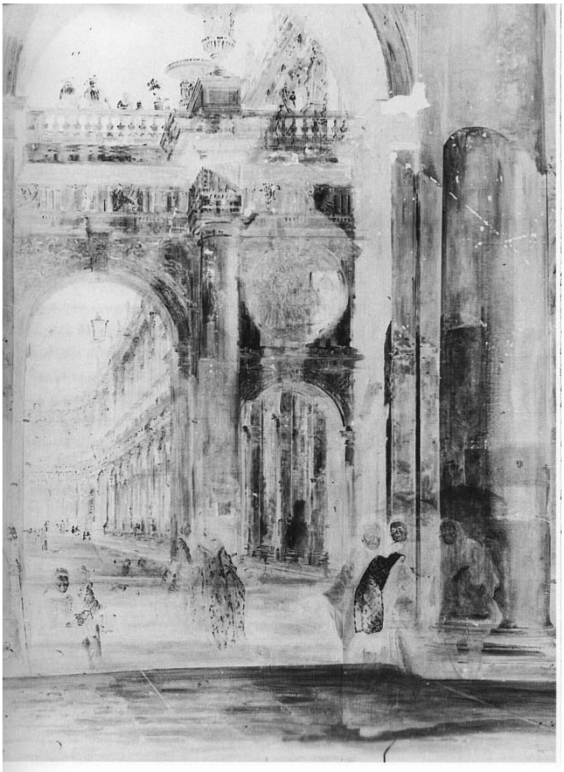


FIG. 2.14. The fourth autoradiograph, with an exposure time of 14 days, of the painting shown in Fig. 2.11.

2.3. CONCLUSIONS

Research on paintings using nuclear methods is important to determine their authenticity and attribution. It reveals the characteristic techniques that typify individual artists and differentiates materials with a long history of use, depending on the place and method of their production. These data objectively supplement the stylistic, iconographic and archival studies conducted by art historians on a work of art.

The large scale use of nuclear techniques has rendered them indispensable tools in studies of works of art and conservation for many years. The results of these analyses are often decisive in determining the attribution and constitute the basis for selecting methods used in the conservation of historical objects. These methods are also gaining recognition among Polish art historians and conservators, following the exhibition at the National Museum in Warsaw[2].

Although the information on the construction of a painting does not always have a direct impact on its humanistic interpretation, it is of basic importance for explaining what methods were used to give paintings their artistic expression. They help in understanding how particular elements of the work contribute to creating the complex structure and how the technological processes contribute to the subtleties of style and determine the final effect of the painting. These nuclear techniques facilitate in separating particular stages of creative work, and thus also in determining the style of thinking that is characteristic of a given painter. These techniques help assess the artists' technical skills and analyse the different artistic methods they used.

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Chapter 3

PROVENANCING OF POTTERY

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3.1. INTRODUCTION

Owing to its favourable properties, investigations of pottery excavated at nearly all archaeological sites are of major importance for archaeological research. Pottery is not only surviving long periods of storage in the ground without decay but also has a limited lifetime of usage, since it breaks easily. Therefore, it permits cultural short term shifts to be monitored and it allows characterization of short periods of ancient cultures. Many archaeological publications concerning pottery demonstrate this fact. Pottery sherds and whole vessels, if found, are optically and haptically analysed and classified according to fabric, form, style and decoration. Once the different ware groups are formed according to certain archaeological criteria, the question arises as to which of these groups have been produced locally and which are imported. This is not always obvious and, in addition, the question arises from where the foreign pieces have been imported. This knowledge will, on the one hand, reveal the range of the local pottery production and, on the other hand, if a provenance determination is possible, show spheres of influence of other cultures and/or trade relations with this place. If a sequence of consecutive strata exists, a chronological typology may also be established. Already more than 120 years ago A. Conze (1831–1914) tagged pottery finds as the ‘Leitfossil’ of archaeological chronology. The study and comparison of pottery, together with all other artefacts excavated at different sites, finally leads to a dense network of related associations and probabilities allowing a description to be made of the history and lifestyle of humans in ancient cultures even from periods without any written records in sufficient detail. It is not surprising that archaeologists at present are increasingly applying scientific methods to validate this network. In view of modern scientific and technological methods currently available, the examination of old artefacts based on mere description no longer seems sufficient or even acceptable.

Besides dating, natural scientific methods applied to pottery are basically used to reassess and refine the classification made by archaeological means. This scientifically assisted classification, given certain requirements, may in the end result in a determination of the producing workshop or, at least, of the producing region. Frequently this process is called 'provenancing' of pottery. Unusual results may point to archaeological misclassifications and/or lead to the identification of forgeries of vases or figurines on the markets. Mainly two approaches are in use for these tasks at present: a measurement of the elemental and especially the trace elemental content in pottery by a chemical analysis method and, on the other hand, a petrographic investigation of the mineral portions in it. Because of the need for a chemical analysis, the first method is applied mainly by so-called archaeological scientists (archaeometrists) in natural scientific laboratories offering the special equipment required. In general, trace elements do not play any role for the appearance, the material properties or the manufacturing process of pottery. These can be regarded as just minor contaminations. Since these contaminations enter pottery mainly through the clay part employed, they indicate the clay bed that has been exploited and, hence, the place of production, assuming that transport of clays over longer distances was not very probable in early times. Ethnoarchaeological studies of modern potters working in a traditional way have demonstrated that most of them obtained their raw material within a distance of no more than 7 km [3.1]. The place of production itself, characterized mainly by this trace elemental 'code', can be recognized if reference material of known provenance from different sites is compared with the piece of questionable provenance and found to have a similar composition to those from one of the sites. Therefore, this method of provenance determination is often termed 'chemical fingerprinting'.

As mentioned above, petrography is a frequently applied method of pottery provenancing. Thin sections of about 30 μm are prepared and placed under a polarizing (petrographic) microscope to identify porosity, texture and particularly the different mineral inclusions, their grain sizes and shape parameters. These visible mineral grains dominate in the non-plastic part of the pottery. They may be occurring naturally in the clay bed or they may have been added and mixed by the potters as tempera. The clay part, the so-called plastic part, has mineral sizes of only about 2 μm, too small to be visible in a petrographic microscope. In this respect, petrography is complementary to chemical analysis, looking at different information stored in pottery sherds. Obviously, it cannot be applied unless significant quantities of such mineral inclusions are present. Again, a comparison with geological reference material clarifies if the mineral content of a vessel agrees with that of a geographical site. In that case, the vessel may have been produced locally at or near the site of the reference. If the mineral content is different, it is likely to originate from a place where these foreign minerals occur.

The method of petrography is employed not only by archaeometrists, but also by many archaeologists, since the equipment needed is often readily available and since archaeologists are already well trained to inspect and compare mineralogical images. Already in 1956, A. Shepard pointed to the relevance of such mineralogical investigations for pottery characterization [3.2]. Petrography is well suited to verify the classification of chemical analyses and/or to define possible subgroups. Similar to other mineralogical techniques such as scanning electron microscopy (SEM) or X ray diffraction (XRD), petrography is also helpful to clarify chemical differences or to learn more about the production techniques of the pottery being investigated, for example, the firing temperature. The best and most comprehensive results can be obtained if, in a so-called integrated approach [3.3], petrography as well as chemical analysis is used. If only a provenance determination is needed, chemical analysis is superior to petrography as it produces hard, quantitative data that can be subjected to rigorous statistical treatment and does not depend on acquired expertise in recognizing inclusions.

3.2. PRINCIPLES OF CHEMICAL PROVENANCING OF POTTERY

Identification of production workshops of pottery by chemical analyses is a well explored and stable field. The principles of provenancing are easily understood, if the method of producing pottery is considered. Ancient potters prepared a large lump of clay according to a certain fixed recipe derived from trial and error or tradition. First, they selected clay from one or, in the case of clay mixing, from several clay beds. Coarse parts if present may have been removed. For highly plastic clay bodies, tempering material may also have been added. Hankey [3.4] wrote pointedly that: “Potters, however, are rather like cooks in choosing ingredients”. The final stage was a well homogenized lump of clay. It is certainly true that all products formed from this well homogenized clay will have the same elemental composition for the major, minor and trace elements. This composition depends on the geochemical composition of the clay bed or beds exploited and on the special recipe used. The manufactured and desiccated pieces were subsequently fired, which does not change the element concentrations. Exceptions are light elements that are not considered in provenancing, such as carbon or oxygen, and only some other special elements such as, for example, arsenic or bromine, which like carbon dioxide may partly escape. Therefore, the composition of fired vessels reflects the composition of the clay paste used and points to the producing pottery workshop. Now, in provenancing, the assumptions are made that:

(a) The reverse is also true: all vessels having the same elemental composition have been produced from the same clay paste available and prepared in a certain pottery workshop.

(b) This paste has a composition that is unique, i.e. it occurs only in the products of this workshop and is different for all other production centres of pottery.

(c) The paste composition can be measured in the final fired products (see Section 3.5.1 for post-depositional changes).

This is expressed in the so-called provenance postulate, originally formulated more than 30 years ago by Weigand et al. [3.5] and slightly modified to consider potters' pastes instead of sources of raw material [3.6, 3.7]: the scatter of concentrations in a certain *paste* has to be assumed to be smaller than the scatter between different *pastes*. Owing to the good homogenization of the clay pastes, this postulate was found to be fulfilled in the majority of cases, as evidenced by numerous measurements of pottery composition. Experience also proves that potters used to follow strictly their once established recipes, since pottery compositions are usually found to be unchanged for longer time periods. This is explainable considering the economic loss occurring if a changed recipe resulted in destruction of part or the whole charge of the kiln during firing.

The uniqueness of an elemental pattern in pottery cannot be strictly proved, but several arguments strengthen this assumption. It is obvious that many 'parameters', i.e. elemental concentrations or other data such as isotope ratios, are needed to characterize a production series from a pottery workshop unambiguously. The more values that are available, the higher will be the probability that a clay paste of another workshop does not incidentally show the same pattern. It is generally agreed that at least 20, better more, concentration values have to be measured to map a specific pattern. In addition, small experimental uncertainties are helpful to differentiate between different patterns. Archaeological knowledge about possible and impossible production sites also limits the number of choices.

To summarize, pottery pieces having the same elemental composition are assumed to have been produced from the same unique clay paste and, since the geochemical compositions of the clays exploited are usually different for different regions, can be assigned to a certain place of production. If at a pottery workshop several different recipes have been in use, different compositional patterns can be measured for one and the same place corresponding to different 'production series' there. On the other hand, if, in a possibly extended region, different workshops used the same geological clay beds and the same recipes, the same elemental patterns are obtained for all these workshops and a definite provenance determination from one single workshop of this group is not possible in that case.

3.3. ELEMENTAL ANALYSIS METHODS

The first publications with data of measured elemental concentrations from a number of pottery sherds already appeared about 50 years ago. At that time, nearly contemporaneously, three methods started to be employed which have contributed most of the results up to the present. These are:

(a) Neutron activation analysis (NAA) [3.8, 3.9];
(b) X ray fluorescence (XRF) [3.10];
(c) Spectroscopic methods such as optical emission spectroscopy (OES) [3.11] or, shortly afterwards, atomic absorption spectroscopy (AAS).

A good overview of these methods and early provenance studies is given in Ref. [3.12]. At present, other methods such as ICP-OS or ICP-MS, or SIMS, to name a few, are increasingly used. A detailed description of these analysis methods is found in many textbooks and will not be given here (see, e.g., Ref. [3.13] or [3.14]).

The requirements essential for any method applied to determining elemental concentrations in pottery are:

(a) High precision (reproducibility): The uncertainties of the measured elemental abundances should be small, to be able to differentiate successfully between different patterns.
(b) High sensitivity: Elements with concentrations down to the trace element level should be measurable.
(c) High versatility: The method should be multielemental, many elemental concentrations should be measurable simultaneously.
(d) High throughput: In provenancing, many samples have to be measured.
(e) Capability to be automated: To reduce the workload, a sample changer and computers should be applicable.
(f) High accuracy: Correct quantitative values will facilitate interlaboratory comparisons.

3.4. NEUTRON ACTIVATION ANALYSIS AND CONCENTRATION DATA EVALUATION

Instrumental neutron activation analysis (INAA) generally fulfils the mentioned properties for provenancing analysis of pottery very well. Each sample, together with samples of a standard material of known composition, is irradiated at a research reactor with neutrons to form radioactive products. The successive, time delayed, decay of these products leads to emission of gamma rays, characteristic of the elemental content of the sample. Semiconductor detectors detect gamma ray intensities in a large energy range and, hence, many elements can be determined simultaneously. The main elements of clays and pottery are silicon, aluminium and oxygen. They form only short lived products and do not interfere with signals from other, longer lived, isotopes of trace elements, providing the high sensitivity needed. Trace elements are important in provenancing, since they are present mainly in the clay part and are less abundant in the non-plastic parts, and it is this clay part that determines provenance. Reproducibility as a function of the experimental counting uncertainties can be improved by a prolonged counting time to be chosen at demand for each sample. Comparison with the gamma ray spectra emitted of the standards permits a quantitative elemental analysis. To facilitate the comparison, samples and standards have to be irradiated, measured and evaluated in the same way.

As an example, for the NAA procedure set up at the Helmholtz-Institut für Strahlen- und Kernphysik in Bonn, a small amount of about 60–80 mg material is needed for analysis of a pottery vessel. Repeated measurements of several samples from the same vessel have shown that in most cases, including relatively coarse wares, this amount is representative of the whole vessel. In addition, the position of sampling on the vessel is arbitrary, supporting the assumption of paste homogeneity. To take a sample, a few samples of pottery removed by pliers are powdered in an agate mortar, or the powder is obtained using a drilling machine with a pure sapphire (corundum) drill bit. Corundum has a hardness of 9 on the Mohs hardness scale, just below diamond. Tungsten carbide drills are as hard as diamond, but are not recommended, since, besides tungsten, measurable contaminations of cobalt and tantalum often occur. In general, a 10 mm diameter drill is used in Bonn. This leads to a shallow mould placed in most cases at the back of a pottery sherd or at the bottom of a whole vessel indicating that this piece was chosen for analysis. To guarantee a fixed measurement geometry, the powder of each sample is mixed with a powder of pure cellulose (60 mg) and pressed into a pill of 10 mm diameter. Each pill is wrapped with a sheet of pure aluminium foil to avoid loss of material. A set of 36 pills is then sent for irradiation to the research reactor at Geesthacht near Hamburg, together with four pills of the Bonn pottery standard of known composition and a blank cellulose pill. The concentrations of this standard have been calibrated with the well known Berkeley pottery standard [3.9] and checked with various commercially available and other standards. The whole set is irradiated for 90 min at a thermal neutron flux of 5×10^{13} n/(cm^2·s). After transport of the samples to the laboratory in Bonn, each sample is measured four times between 5 and 24 days after the end of irradiation. Measurement times per sample vary between 2000 and 5000 s. These measurements are described at length in Ref. [3.15], where a list of the different gamma lines evaluated in Bonn can also be found. In Fig. 3.1, two gamma ray spectra emitted from the same sample at two different decay times are shown. To obtain precise concentration values, the measured gamma ray intensities have to be corrected for:

(a) Background correction: The background intensities from the wrapping foil, the cellulose, the laboratory walls and the cosmic radiation, visible in the blank cellulose sample, need to be subtracted.
(b) Dead time correction: During the measurements of the sample and the standard, count rate depending on different dead times of the gamma ray detector have to be considered.
(c) Matrix absorption corrections: With a sample thickness of about 1 mm, these are only important for gamma ray energies of less than 50 keV, which are rarely evaluated.
(d) Corrections of individual gamma ray intensities due to gamma line interferences: Different nuclei may emit gamma rays with quite similar energies overlapping in the spectra. See as an example of this type of correction the 320.0 keV line of ^{51}Cr in Fig. 3.1. It covers a hidden 319.4 keV line of ^{147}Nd. The intensity of this line can be calculated from the intensity of a monitor line of ^{147}Nd at 531.0 keV.
(e) Corrections due to nuclear reactions: They occur if not only low energy neutrons but also neutrons with higher energies are present at the irradiation position: for example, the chromium content is determined by the decay of the radioactive ^{51}Cr isotope (gamma energy of 320 keV), which is produced by low energy neutrons from the ^{50}Cr in the sample, but also by high energy neutrons from iron according to the nuclear reaction ^{54}Fe(n, α)^{51}Cr, so the iron content of the sample influences the chromium result. Measurement of a pure iron sample without any chromium at unchanged irradiation conditions can be used to determine this correction.
(f) Corrections due to the induced fission of ^{235}U: for example, zirconium is produced as a fission product in amounts which, in dependence on the uranium concentration, may falsify considerably the real zirconium content in the sample. Again, a measurement of a pure uranium sample is needed.

For each irradiation position in the reactor and for each geometry and detector system, all these corrections have to be determined before starting the analysis of the samples under research. The measurement of four spectra of each sample in Bonn allows many concentration values to be determined repeatedly on the basis of different gamma lines and the results to be confirmed. In Table 3.1, redundant data of selected elements measured for a sample from Emecik (see archaeological example below) are shown as an example. The final result of the

TABLE 3.1. SOME ELEMENTAL CONCENTRATIONS (μg/g)

Element	C	δ	Element	C	δ	Element	C	δ
CoA1	22.668	0.472	HfA2	4.892	0.371	ThA3	11.279	0.352
CoB1	23.341	0.408	HfA3	4.465	0.229	ThB3	12.225	0.410
CoA4	23.405	0.106	HfB4	4.639	0.064	ThC3	11.659	0.511
CoB4	23.246	0.109				ThA4	11.817	0.062
			ScA1	16.638	0.040	ThD4	11.410	0.364
Cr 1	306.400	3.618	ScB1	16.687	0.060			
Cr 2	321.484	10.020	ScA4	16.656	0.021	U A1	1.875	0.086
Cr 3	300.452	7.433	ScB4	16.630	0.023	U B1	1.951	0.088
Cr 4	329.971	1.545				U C2	1.975	0.087
			SmA2	5.085	0.021			
FeA1	4.724	0.063	SmB2	5.240	0.053	YbA1	2.557	0.057
FeB1	4.564	0.052	SmC2	5.095	0.022	YbC1	2.717	0.119
FeD2	4.437	0.488				YbA2	2.770	0.208
FeD3	3.998	0.357	ThA1	11.746	0.157	YbB2	2.917	0.228
FeA4	4.630	0.020	ThA2	12.528	0.526	YbB3	2.593	0.161
FeB4	4.629	0.017	ThB2	13.895	0.685			
FeD4	4.522	0.117	ThC2	12.906	0.845			

procedure is the elemental composition pattern of each sample. The elements Co, Cr, Fe (in %), Hf, Sc, Sm, Th, U and Yb for the sample EME-C 1 (see Fig. 3.9) and their measurement uncertainties δ (counting errors) are given. At the third position after the element name, a letter describing the specific gamma line and at the fourth position the measurements Nos 1–4 are given. The spectra depicted in Fig. 3.1 show the chromium line of measurements Nos 1 and 4 evaluated here as an example. Many other elements can be determined or manifold as well. Most values agree inside their measurement uncertainties well. In the laboratory at Bonn the concentrations of up to 30 elements, if present above detection limits, can be determined with the NAA procedure described. Since measurements start at five days after the irradiation, short lived isotopes cannot be determined and other elements such as, for example, calcium at low concentration levels can only be determined with large uncertainties.

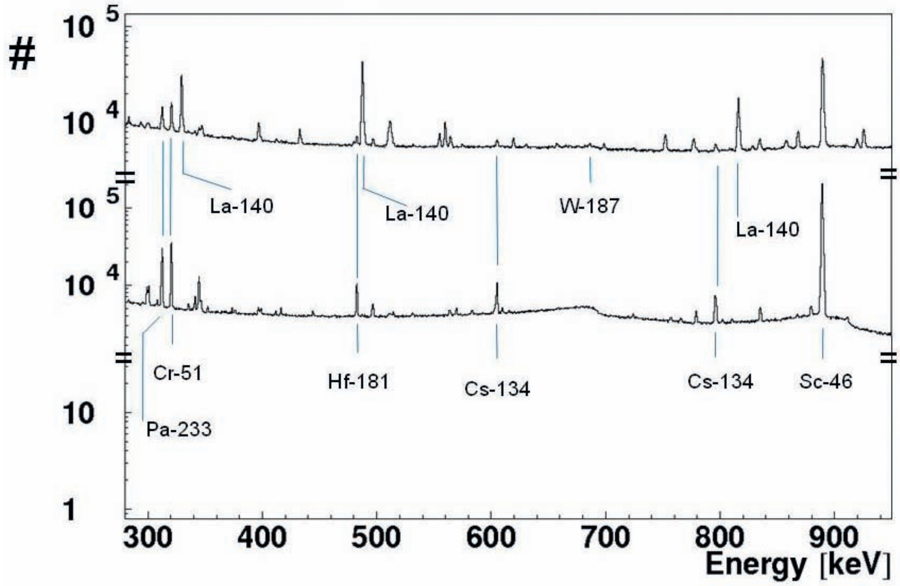

FIG. 3.1. Part 280 keV–950 keV of the gamma ray spectra of a pottery sample. The measurement No. 1 (top) at five days and the measurement No. 4 (bottom) at 24 days after the irradiation are shown. Short lived isotopes such as ^{140}La in measurement No. 1 conceal the lines of trace elements with low intensities. They are well resolved in the late measurement, No. 4.

3.5. CONCENTRATION DATA COMPARISON AND PATTERN RECOGNITION

3.5.1. Conventional methods

The next important step in provenancing is the formation of groups of samples having similar elemental patterns and, thus, the same origin. At first the question of which elements should be chosen for the comparison has to be addressed. As mentioned above, arsenic and bromine concentrations can change during firing of the vessels. Further changes may occur during long time deposition of the items of pottery underground. Especially barium and calcium and sometimes the alkali elements sodium, potassium, rubidium and caesium may be affected, and the concentrations measured in pottery sherds may be different from the concentrations in the clay paste [3.16]. If the potters at a workshop used different paste preparation recipes, removing or adding non-plastic material such as sand or calcite, also the elements in these minerals (mainly silicon, aluminium and calcium) may vary. All these elements have to be handled with care in comparing the patterns and, for the time being, should not be considered. Using INAA, there are many more trace elements determined that have a high probability to reflect the clay composition unaltered.

If the measurement precision is high and the number of samples is not too large, the comparison can be performed simply ‘by hand’ by looking at the measured numbers. Obviously, differing concentrations directly attract attention. However, if the total number of samples or concentrations is larger than 15–20, this approach becomes more and more cumbersome. Consequently, different statistical computer based methods are now employed.

These procedures are best explained in view of a concentration space. If, for a sample concentration, values of three elements are available, they can be depicted as a point in a three dimensional space with orthogonal coordinates corresponding to the concentrations of these three elements as shown in Fig. 3.2. It is obvious that other samples with similar concentrations of these three elements will fill in positions not far away from that point. If now in each sample a number of *m* (instead of just three) elemental concentrations have been determined, each sample can be visualized as one point in an *m*-dimensional space, also termed ‘hyperspace’. And again, points close to each other have similar composition and form ‘clouds of points’ in this hyperspace. Several statistical methods can be used to search in this hyperspace for such clouds. They have been described previously [3.17] and all of them lead to a reduction of the dimensions relevant to solve the problem. A new method will be described as preferred in Bonn below; hence, the standard methods will only be described briefly. In principal component analysis (PCA), the coordinates are mathematically rotated in such a way that the main (first) axis points into the direction of the largest extension (variance) of the whole data set, the second, orthogonally to the first, to the direction of the next largest extension and so forth with decreasing variance. Consider the simple case of only two well separated clouds of points. Here, the main axis will be directed along the connecting line between the clouds to cover most of the total variance. The second axis, perpendicular to the first, will point to the largest variance in that direction, reducing the multidimensionality of the hyperspace to two dimensions. In more complicated cases, with a higher number of groups, axes of higher orders have to be considered. A first complication arises because the concentration values vary widely, from per cent for the main elements down to ppm (parts per million = μg/g) values for trace elements. Therefore, before a statistical data evaluation, a transformation is often done as for example ‘autoscaling’ (average concentration of all data is equal to 0, standard deviation is equal to 1) or ranging (all values are in the range 0–1).

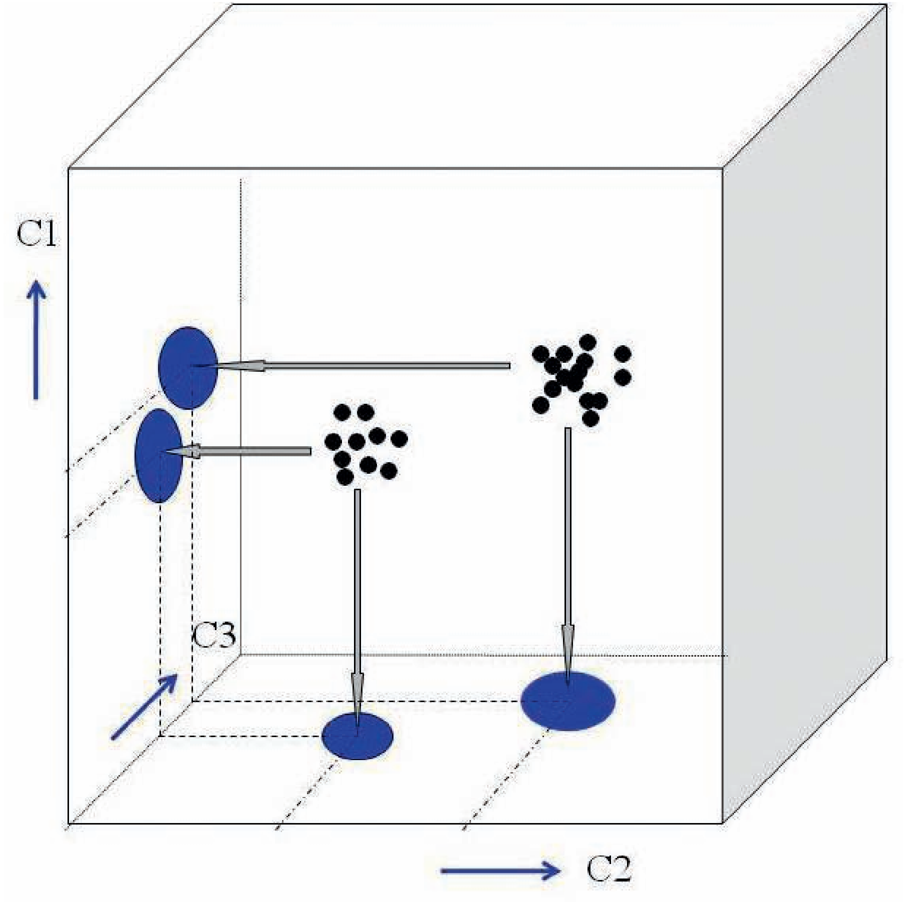

FIG. 3.2. Three dimensional schematic model of the concentration space with 'clouds' of data points. These points correspond to pottery samples of similar elemental compositions of the three concentrations C1, C2 and C3. The extension of the clouds in the direction of the concentration axes depicts the scatter of the data for these concentrations, respectively. Projections of the data on to the C1–C3 and C2–C3 planes are also shown.

Another statistical procedure often employed is hierarchical cluster analysis (CA). Using a certain similarity measure, also called 'distance' (such as the simple squared Euclidian distance between points), here all distances between the single points are calculated and the two closest points are unified to one point. This procedure is repeated until all points are unified into one single point. Besides the choice of a distance, a 'cluster criterion' also has to be defined. This classifies the operation, how a distance of a point to a group of already merged points should be calculated (centroid: distance to the midpoint; single linkage:

distance to the nearest neighbour; complete linkage: distance to the furthest neighbour; average linkage: average value of all distances; Ward method: sum of squared distances to the centre point is minimal; etc.). The protocol of these calculations can be presented as a two dimensional diagram. The individual samples are listed on the horizontal axis, the distances of the successive unifications are given on the vertical axis. A simple example is shown in Fig. 3.3, where the vertical axis is plotted logarithmically. Since this diagram looks like a tree upside down with three main branches (the stem is not shown), the results of a CA calculation are called dendrograms. They reflect the structure of the data points in hyperspace, suggesting the presence of three groups in this example. However, generally, with more complicated structures an interpretation of such dendrograms is difficult. The vertical axis describing relative distances does not specify the compositional similarity of the samples. It is not known how many different groups corresponding to different clay pastes are present in the data set. In an extreme case, all samples might belong to only one group and the structure seen is due just to experimental uncertainties, or, vice versa, all samples might have different origins. It may help to include in the calculations a set of repetitive measurements from the same material, for example, the results of a reference material available in most laboratories. The distance where the data of the standard merge determines a lower limit: groups of pottery with the same origin must merge at larger distances. In Fig. 3.3 the centre group is formed by a set of

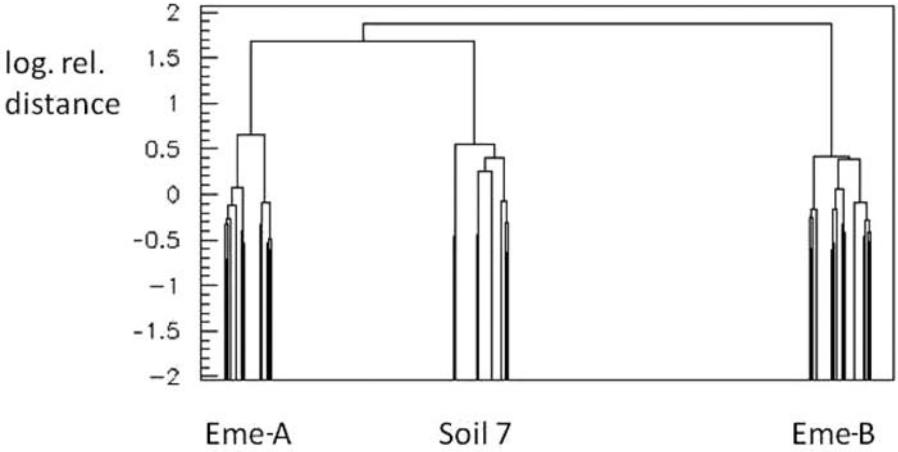

FIG. 3.3. Dendrogram as the result of a CA calculation of a set of 61 samples from the Emecik excavations (see example below) and, in addition, of 32 samples of the IAEA standard material Soil 7. As similarity measure, squared Euclidian distances with 27 elemental concentration values have been chosen. The vertical axis is plotted logarithmically.

measurements of the IAEA reference material Soil 7 [3.18]. Therefore, each of the two other groups shown (EME-A and EME-B) can be assumed to be pottery groups of the same origin and, for example, group EME-A should not be subdivided into two subgroups as suggested in the dendrogram. Further complications arise because the CA (like the PCA) is project oriented. The addition of more samples will change the overall variance of the data set and may produce different results. The same is true for outliers, i.e. single samples with one outlying element concentration. Therefore, such outliers should be identified and removed before a final CA calculation. This is demonstrated in Fig. 3.4, which depicts the dendrogram of the same data without the Soil 7 results. The sequence of the groups has changed. On the basis of earlier calculations including the reference material, it can be concluded that the formed subgroups are not real in this case. Just two groups exist. Calculations with different similarity measures and different cluster criteria should be performed to test whether the CA calculations produce the same results.

3.5.2. The ‘filter’ grouping procedure

Owing to difficulties in the interpretation of dendrograms, but particularly because these CA calculations are unable to consider two details important for evaluation of concentration data from pottery, CA cannot be generally recommended. The first detail concerns the measurement uncertainties which are different for each element concentration using NAA and which are not taken into

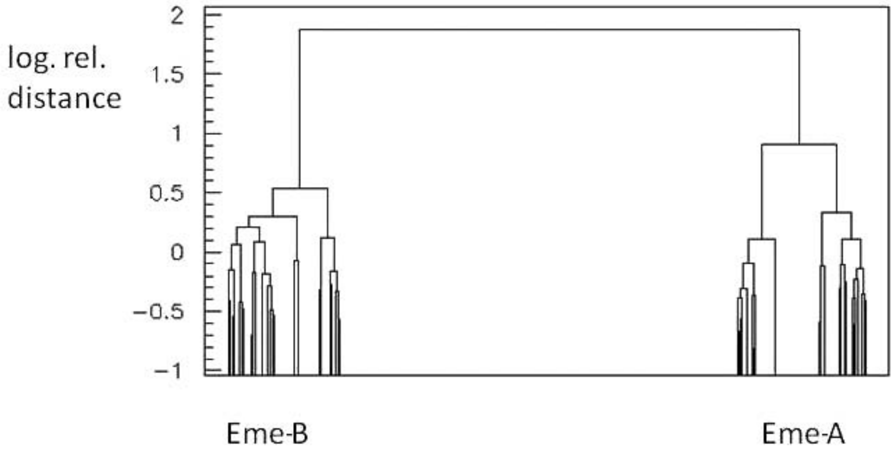

FIG. 3.4. Dendrogram as in Fig. 3.3, now without the IAEA soil 7 samples. The subgroups of the two main groups are not real, but due to the measurement uncertainties.

account by CA as well as PCA calculations. Measurement uncertainty strongly influences the grouping results, as can be seen from the following simple example: the results of 4.0 ± 1.0% and 5.0 ± 1.0% overlap and are statistically not different, but values of 4.0 ± 0.1% and 5.0 ± 0.1% differ by seven standard deviations and indicate clearly different clay pastes. Therefore, measurement uncertainties should be included in the statistical group forming process of pottery samples. The second important detail relates to the human factor. During the preparation of the clay paste, potters may have varied their recipes slightly, taking a little more or less non-plastic material such as sand or calcite or adding tempering material in slightly varying amounts. Consequently, all element concentrations, particularly the trace elements in the clay, may vary by a constant factor, since the non-plastic temper is generally much poorer in trace elements. This is well known as a ‘dilution effect’ of all the elements not present in the diluent [3.19]. This dilution can be corrected for by multiplication of all concentrations of a sample with a constant factor calculated from a best relative fit of the data of the sample with respect to another reference sample or to the mean of the whole group. The dilution correction normalizes differently diluted samples to the same amount of clay parts. It also corrects experimental errors such as neutron flux variations during the irradiation, standard or weighing errors during sample preparation, or weight errors due to different water contents of different samples. In many published bi-plots of elemental concentrations, an elongation of the values of a group of pottery samples from lower to higher values can be seen. In Fig. 3.5(a) such a bi-plot of the raw data of the rare earth elements (REEs) lanthanum and europium is shown, suggesting a positive elemental correlation. After a dilution correction has been applied, the correlation almost disappears and much smaller spreads are obtained as depicted in Fig. 3.5(b). In the PCA and CA calculations such dilution effects can be included, if instead of the concentration data, concentration ratios are used.

How dilution effects and the experimental uncertainties mentioned above can be included in a statistical grouping procedure was shown by Beier and Mommsen [3.20], see also Ref. [3.21]. This procedure acts like a filter in hyperspace. It sorts out of a large databank all samples of a similar composition to a given concentration point or group of points. In general, it tests the hypothesis: ‘this data point belongs to that group’, and this hypothesis is by statistical means either accepted or rejected. As a similarity measure, a modified Mahalanobis distance is calculated that is able to take uncertainties into account. This corresponds to the distance of a point ± its uncertainty to another point ± its uncertainty in units of the average uncertainty in the direction of the connecting line. Instead of a single point, a group of points can be inserted considering now its extension (spread σ = root mean square deviation) again in the direction of the

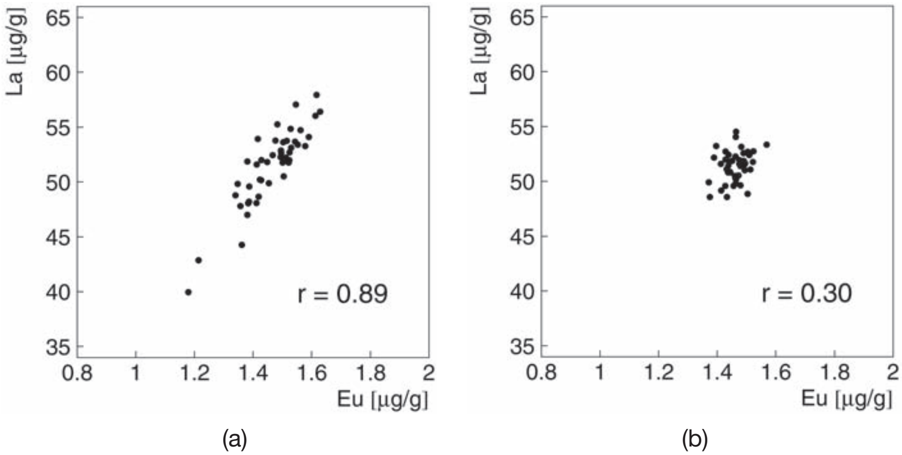

FIG. 3.5. Bi-plot of concentration data of the elements lanthanum and europium for a group of pottery sherds from the Kalabaktepe workshops at Miletus, Turkey. Shown are: (a) the raw data with a correlation coefficient r = 0.89 and (b) the same data after the individual samples have been corrected for dilution using all elemental values resulting in a reduced correlation coefficient and smaller spread of the data.

connecting line in hyperspace. This normalization to the measurement uncertainties or spreads has the advantage that the modified distances can be easily converted into a 'probability of chemical agreement' if a normal distribution is assumed. Even moderate deviations of normality do not change these arguments. Usually we choose the 95% confidence limit (2σ) of group membership as cut-off distance for a group separation or a rejection of a single sample. For about 25 elements, this corresponds to a modified distance value of about 1.6. In contrast to the usual CA calculations, this helps to decide how many statistically separable clusters are present in the data set.

In addition, a best relative fit to correct for possible dilutions is always performed when modified distances are calculated. This results in pottery groups with reduced spreads of the concentration values, i.e. in better defined 'sharper' group patterns. For example, the group EME-A has a mean iron concentration of 5.1 ± 0.5% that is condensed to 5.1 ± 0.2% (see Table 3.2), after average means and spreads are calculated including the dilution correction for each sample. In Fig. 3.6, the histograms of the modified distance values of all the pottery group EME-A samples from the large databank of Bonn University are shown, with and without dilution corrections. This final group EME-A was formed after the following fixed iteration procedure. Starting with one arbitrarily chosen sample as a filter point in hyperspace, all samples with small modified distances were determined and a preliminary group was formed. Using the new average

TABLE 3.2. CONCENTRATION PATTERNS OF THE LARGER GROUPS OF THIS STUDY[a]

	EME-C 12 samples Factor 1.0		EME-B 29 samples Factor 1.0		EME-B′ 6 samples Factor 1.05		EME-A 32 samples Factor 1.0		CYP-I 8 samples Factor 0.83	
Element	*M*	σ (%)	*M*	σ (%)	*M*	σ (%)	*M*	σ (%)	*M*	σ (%)
As	10.6	44	6.54	28	6.74	23	8.47	19	—	
Ba	487	9.7	498	14	504	14	441	24	500	56
Ca (%)	3.84	35	5.54	20	5.68	16	9.95	19	6.89	35
Ce	97.0	3.8	69.8	2.8	66.8	3.0	34.5	3.5	35.8	1.9
Co	30.2	6.1	39.1	7.3	50.4	7.6	26.8	3.3	25.7	5.3
Cr	322	8.2	393	14	574	2.9	311	22	252	13
Cs	12.7	9.2	7.77	15	6.98	10	3.26	9.8	3.60	6.5
Eu	1.34	5.4	1.13	3.5	1.13	2.4	0.86	4.3	0.86	3.4
Fe (%)	5.26	3.5	5.10	3.3	5.58	2.4	5.07	3.4	4.77	4.5
Ga	26.5	10	19.6	11	19.7	13	16.1	11	13.2	25
Hf	6.79	5.3	4.59	4.3	4.36	5.0	2.82	8.3	2.80	6.0
K (%)	3.31	9.7	2.17	8.2	1.96	3.5	1.45	9.9	1.67	12
La	46.5	5.9	34.1	2.7	33.1	2.8	16.1	3.6	17.2	2.7
Lu	0.55	4.2	0.46	7.7	0.44	6.9	0.35	5.4	0.34	8.1
Na (%)	0.78	21	0.62	13	0.63	16	0.87	11	1.03	13
Nd	36.9	10	27.4	8.3	26.0	7.4	14.7	10	16.3	9.6
Ni	280	20	407	16	648	11	214	18	229	6.8
Rb	170	5.2	113	13	102	6.3	52.6	10	58.9	12
Sb	0.79	17	0.75	22	0.81	18	0.60	23	0.76	16
Sc	20.6	2.2	18.0	3.1	18.5	1.8	21.3	5.1	19.6	5.7
Sm	6.36	7.7	5.01	5.2	4.67	11	3.05	4.1	3.14	6.1
Ta	1.30	3.6	0.98	4.1	0.93	4.2	0.53	6.0	0.54	6.9
Tb	0.81	9.2	0.69	7.3	0.70	11	0.50	10	0.51	7.6
Th	16.7	2.7	12.8	2.0	12.2	3.4	5.50	4.6	5.61	2.6
Ti (%)	0.57	12	0.47	18	0.53	16	0.52	19	0.40	24
U	3.16	6.4	2.23	5.2	2.09	4.9	1.60	14	1.75	19

TABLE 3.2. CONCENTRATION PATTERNS OF THE LARGER GROUPS OF THIS STUDY[a] (cont.)

	EME-C 12 samples Factor 1.0		EME-B 29 samples Factor 1.0		EME-B′ 6 samples Factor 1.05		EME-A 32 samples Factor 1.0		CYP-I 8 samples Factor 0.83	
Element	M	σ (%)	M	σ (%)	M	σ (%)	M	σ (%)	M	σ (%)
W	3.03	8.9	2.24	13	2.28	7.0	1.48	15	1.32	17
Yb	3.71	4.6	2.88	3.2	2.82	2.1	2.04	5.0	1.97	2.4
Zn	109	16.0	98.3	15	101	26	96.5	12	83.4	6.9
Zr	217	18	141	20	135	23	86.6	36	126	19

[a] Shown are the average values M of the groups in µg/g (ppm), if not indicated otherwise, and their spreads (root mean square deviations) σ as a percentage of M. The individual data sets of the samples have been corrected for constant shifts of the concentrations (best relative fit with respect to M). To show the close similarity of subgroup B′ to B, pattern B′ has been multiplied by a best relative fit factor of 1.05, and analogously EME-A to CYP-I, by a factor of 0.83.

concentration values and their spreads, more samples were found fulfilling the membership criterion. The procedure continued, more and more samples were added, until the whole group of neighbouring samples was detected and included in the group. Not all the elements were taken into account. Sodium, for example, or arsenic are very precisely measurable with NAA, but there is usually a wide scatter in their concentrations in otherwise well defined groups of pottery. Since the modified distances are normalized to the uncertainties, samples with sodium or arsenic concentrations differing from the filter point would be statistically sorted out and missed as members of the group. In addition, elements such as calcium, which are often part of a diluent, are not taken into account when the dilution correction is calculated. On the other hand, elements well suited for provenancing, but measurable only with large uncertainties can be included in the group forming procedure.

There are several additional advantages of the filtering procedure. The raw data can be used directly, no data transformation is needed. Very large databanks of several thousand samples can be studied. Additionally, samples added later will not influence the results if they do not belong to one of the groups of the study. Missing concentration values are not perturbing; the calculations can be done for these samples in a reduced hyperspace. At Bonn University, such repeated calculations have always been performed for each sample as a test for erroneous data, leaving out the most deviating element, respectively, with the

```
Number of samples            (a)
   |                                          O  C   COF K   T K S
   |                                         CC CC C SCA F F A AAA
   |                                  C   C  CCCZC C CAC F A K CVA
 10+                                  P   CC CGGADCCCZKL F C F FFL
   |                                  F   TC CAFAFCOOCFG PFF G KTF
   |           F         C            C  CPS CADRACAAFAA AKTCT LTG
   |           C         C    C F    FFC CPC ZPDRAAKCFAT AATCTGTAO
   |     X     C  C  E   S    C C    CCC CARCOAPGKATFTAT APTCAGFPK
  5+     X     X  CCXC   C  C SCCC   CCC CFRCFAAKACAAFAFCAATAAVAAT
   |    XX     FF CCZC   Z  F SXFS   FEFZFAFSAFAPAAAAAAAAKAAGAPAAA
   |    XXX   CXC XXXC   ZCCCCCCCFC CVGCAVATGAAAPAAAAAAAAAAATAAAAA
   |   XXXXC CXFFFXXFZ CCCCCFCFCACKCSVKGAFAPXAAAPAAAAAFAAAAAAAAAAA
   | XXXXXXX XXFCXFFFF ZFCCCCCCCAPTCGFGGAAAAKAKAAAAAAAAAAAAAAFTAAA
  0+----+----+----+----+----+----+----+----+----+----+----+----+--
   0    1    2    3    4    5    6    7    8    9   10   11   12
                    Modified Mahalanobis distance
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```
Number of samples            (b)
   |                      CCFKSCAKTTTTATDAAPAFKAAALAFAMAATAMFMAAAM
   |                     CCSCGSCTATKTTDGLAPKAATAAGAALAALAMTKAMAAAT
   |  X                C CCCCGCSTFTGTTFTKFFPTTKAATAAAKAFAFTATMAAAA
 10+  X                S CFFZGCCTTTGTGLPTAAAAAAAKLAAAFAMAAAAMMKAMA
   |  X             C  C CCCCKFKTTTTTTLPDKAFAAALTAAAFKAMAAAAMGMAAA
   | XX      E     CC  FFSFCCGEGTTTTTTTGTAAAAAATFAAMAALAAAKCFAAAAA
   | XX      CCF  CCZ CCSFCKFTCKTTTFTOPKTAAATAALAAATAMAAAACAAGAAGA
   | XX X    CCC  CCZCCCFECKGFCTFTPTFPAKKAAKAAAAAATAAMFAMAPAAAAAAA
  5+ XXXX    FCCCCCCZCZFKCCGGTLTTTVTOFFKAAAKAAAAAAAAAAAAAAKKAAFAAM
   | XXXX CC CCCZCCZCVCGCCTCGTTPPAAAAAKAAAALAAFKAAAATFAAATMAMAFKAA
   | XXXX CCCFVCZFCZCCCVCGTTTTAAPATAAAKAAAAAAAAAAAAAFGAFAAAAAAAAAK
   | XXXXXXCCFVEVFCZVFGVGCTKKFKKAFAAFAFFAAAAGAAAMAAAAAKAAAAAAAMKAA
  0+----+----+----+----+----+----+----+----+----+----+----+----+--
   0    1    2    3    4    5    6    7    8    9   10   11   12
                    Modified Mahalanobis distance
```

FIG. 3.6. Histogram of modified Mahalanobis distances calculated in the 27 dimensional hyperspace from the centre point of group EME-A: (a) without the dilution correction and (b) after this correction has been applied[1].

highest contribution to the modified distance value. For good members of the group, the modified distance values will decrease fast and steadily, whereas for members on the borders of the group (cloud of points), the distance values will remain around the limiting value of 1.6 and their addition to the group is questionable. An example of a sequence of decreasing distance values, when the

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[1] In case (b), all 32 samples of this group from Cyprus, designated by the letter X, have modified distance values of ≤1.6 (see text). The sample with the largest distance in case (a) matches this group statistically if a dilution correction of 24% (best relative fit factor of 1.24) is applied. A second group C of samples from Cyprus is just separable from group EME-A.

dimensions of hyperspace are stepwise reduced, is given in Ref. [3.22], p. 19. Erasing a single outlying concentration will result in a sharp drop of the modified distance value from a high value to below 1.6, indicating that all other element concentrations match the group. It can be marked as an outlier, caused with high probability by an unrecognized contamination or a measuring/spectrum evaluation error.

As the final result of every statistical evaluation, the elemental patterns of the groups formed should always be given. An inspection of the average concentration values and especially of the spreads or variances of the individual elements can serve as a check if the grouping is good and valid. Large variances of single elements, if not explainable by manufacturing characteristics during the preparation and homogenization of the clay paste, may point to possible undetected subgroups and perhaps the need to re-evaluate the data.

3.6. REFERENCE MATERIAL

Following a successful grouping of pottery samples from a site, a useful archaeological result can be cited: all members of each group are assumed to have been produced using the same clay paste and, therefore, should have the same geographical origin. For identification of the producing workshops, further work has to be conducted. To determine the local paste composition(s), so-called ‘reference materials’ from well defined production localities need to be analysed. Identification of good reference material is the greatest problem of provenancing, given the numerous workshops producing pottery in ancient times. The analysis of clays from a region may be helpful, but very often is not successful. Mostly, the clay beds exploited in ancient times are not well known now. Eventually, they may no longer exist, may be exhausted or covered with later sediments. In addition, the raw clay composition is in most cases different from the composition of the pastes prepared by the potters. Only when clay is found readily prepared for use, will the composition agree with that of the finished pottery. However, such pieces of known origin are rare and difficult to find. If a kiln site has been excavated including the waste heap of the kiln, the problems are solved: the rubbish will show the elemental pattern of the pastes in use there. Frequently, ancient kiln sites have not been located. Disposal sites found in a settlement context may contain kiln refuse, but the contents may also result from destructive fires of imported vessels. Without undisputed reference pieces, distribution arguments have often to be relied on. If, for example, a pattern is found in many pieces at one site and not in great numbers somewhere else, the assignment of this pattern to this site seems probable. Considering the limited number of analysed samples, they all might have been imported to the site.

However, the argument of a local production at a site is strengthened if the time span of existence of a pattern at the site is large. Imports at very different time periods from the same workshops to the site are not highly probable. Additionally, if very different ware types such as loom weights, bricks, roof tiles, coarse cheap vessels and also expensive rare vessels of high quality are members of the group, the probability of local production of all these pieces is increased. In general, a large number of samples have to be analysed for a successful provenance determination of pottery. The larger the accumulated databank of a laboratory, the higher is the chance to obtain good and reliable results.

3.7. EXAMPLE: POTTERY FROM THE APOLLON SANCTUARY NEAR EMECIK VILLAGE ON THE KNIDIAN PENINSULA (TURKEY)

Beginning in 1998, the archaic Apollon sanctuary near Emecik village on the Knidian peninsula (see Fig. 3.7) was excavated by a German–Turkish team [3.23]. The sanctuary was constructed on an artificially created terrace bordered

FIG. 3.7. Map of the Knidian peninsula in the eastern Aegean.

by a wall with a height of about 5 m. This wall can be dated to about 550 B.C. The material behind the wall was filled up to construct the terrace. The excavations in this area brought to light a large number of archaic Greek pottery sherds dating to the time period about 650–550 B.C. As all pieces were found in this intermixed fill, a stratigraphically based chronology for the archaic ceramics was not possible. It can be assumed, besides local material, many pieces have been imported and presented as votive gifts to the sanctuary. The sherds have been grouped by archaeological means into several ware types: transport amphoras, fine wares as flat plates decorated with ornamental and figurative motifs (flowers, animals and mythological creatures), relief pithoi and amphoras, a large number of local or imported terracottas used as votive offerings (mainly bull figurines, male and female votive bearers), orientally decorated jugs and open vessels, dinoi[2] with their stands and several further, probably imported, ware groups including wild goat decorated Ionian jugs and Attic vessels such as large dinoi. The main aim of this archaeometric project was to classify these sherds chemically, to compare these chemical groups with the archaeological classification and, thus, to obtain new results on East Dorian pottery production. Furthermore, a comparison of these results with the ceramic material of other find sites in our databank may reveal imported ware types and their origin. Therefore, a representative selection of these wares has been chosen for NAA. Since the Bonn NAA databank now contains more than 8000 samples from Greece and the Eastern Mediterranean, the chance to identify known elemental patterns has been considered to be reasonable.

The 124 sherds selected for analysis came from the sanctuary at Emecik (101 samples) [3.24], from the dump heap of the pottery workshop at Resadiye (12 samples) [3.25] and from the collection of archaic finds of Old Knidos in the 'Antikensammlung der Staatlichen Museen' in Berlin (11 samples) [3.26]. As presented to the Bonn group before our analysis, their archaeological grouping according to ware types is given in Table 3.3, column 1.

3.7.1. Results of the chemical analyses

The search for sherds of similar chemical composition was done using only the raw data, without considering the archaeological classification. The search revealed — besides a number of chemical singles and a few imported pieces — the presence of a number of groups called EME-A, ... , EME-G. All these compositional groups were new to us. This result was expected, since we

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[2] Dinos (plural: dinoi) is a type of Greek vase. It is formed of a large bowl with a rounded lip. Dinoi had a special status when they were used.

TABLE 3.3. ARCHAEOLOGICAL CLASSIFICATION OF THE 124 SHERDS FROM EMECIK, OLD KNIDOS, AND RESADIYE COMPARED WITH THE CHEMICAL GROUPING

(listed are the numbers of group and (+) of associated members)

NAA groups EME-	C	C′	B	B′	D	E	D	G	A	A′	Other	Singles	Totals
Archaeological classification	Local		Local?		Unknown				Cyprus?				
Local amphoras	10	2				1						1	14
Local decorated fine ware	2		26 + 3	4 + 1	3	2		1	3			1	46
Local relief vessels				1			1	4 + 2				2	10
Terracottas			2	1		1	5	2	29 + 1	2		3	46
Ionian jugs			1			1					4 (from Miletos)		6
Attic vessels											2 (from Miletos)		

did not have material from the Knidian peninsula or other parts of a Dorian region before. The distribution of the group members into the archaeological groups is shown in Table 3.3. Samples are associated with a group if they deviate in one or two concentration values only. They might belong to the group, but they could also be first members of a hitherto unknown group of different origin. Table 3.2 gives the average concentration values of the larger groups and their spreads (variances are root mean square deviations in per cent). Associated group members are not included in these patterns. All the different groups are well separated as demonstrated also in Fig. 3.8, where the result of a discriminant analysis is shown taking the 112 samples, which are group members, including eight samples of a group CYP-I from the Bonn databank (see below) assuming a distribution into 11 clusters. Except for arsenic, barium and sodium (see above), all the elemental values as given in Table 3.3 have been used for this calculation.

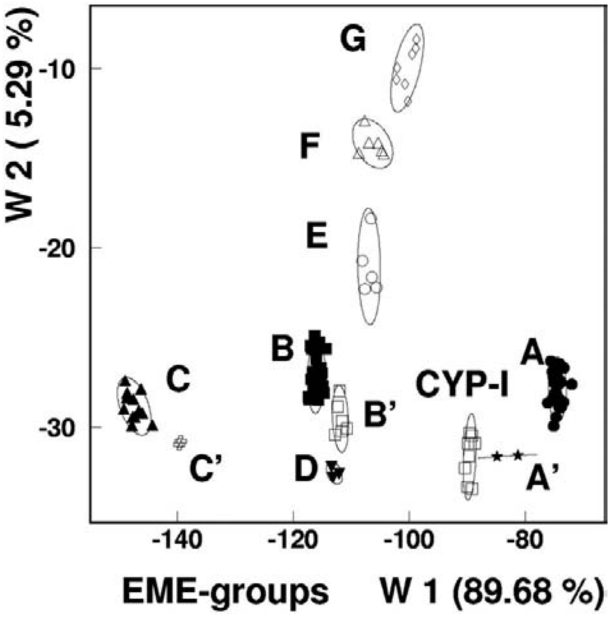

FIG. 3.8. Result of a discriminant analysis of the 112 grouped samples including eight samples of group CYP-I and assuming 11 clusters[3].

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[3] Plotted are the discriminant functions W1 and W2, which cover 90% and 5%, respectively, of the between-group variance. The ellipses drawn are the 2σ boundaries of the groups. The different groups are well separable.

A definite assignment to a local production is possible only for group EME-C and subgroup EME-C′, a pair of samples, since all (except one single) sherds of the kiln material from Resadiye belong to this group. The main part of the fine ware samples of different forms, archaeologically considered as locally made products, belongs to group EME-B and its subgroup EME-B′. This subgroup is very similar to group EME-B, but diluted by 5% (best relative fit factor with respect to $B = 1.05$) with increased iron, cobalt, nickel and chromium concentrations. Since until now both chemical patterns have not been found anywhere else and since they are so abundant at Emecik, a local production source can be suggested. An example of a sherd belonging to the group EME-B is shown in Fig. 3.9.

The numbers of the members in the other groups EME-D, -E, -F and -G are much smaller. These vessels might represent different local clay pastes or they

FIG. 3.9. Fragment of a plate depicting a ship (sample EME-C 1), seventh or sixth century B.C., NAA group EME-B: East Dorian, probably local Knidian origin.

might have been imported from somewhere else. Archaeometrically, similar to chemical singles, nothing can be concluded for these small groups without further material given to Bonn University for analysis. Figure 3.10 shows a sherd of a local relief amphora of group EME-G that is archaeologically considered to be of Dorian, probably local Knidian, origin.

In the case of patterns EME-A and EME-A′, although new to the Bonn group, our databank gives a hint. These patterns, found mainly in the terracotta fragments, have a general Cypriot composition. In Fig. 3.11, a fragment of a human figure of this group is depicted. The concentrations are not very different from several Cypriot patterns in our databank and especially close to the group CYP-I, but they are very different from all our Greek and non-Cypriot Eastern Mediterranean patterns. In Table 3.2, pattern CYP-I, multiplied by a factor of 0.83, is compared with pattern EME-A. CYP-I is known to represent with high probability a Cypriot paste used during Mycenaean times [3.27, 3.28]. The paste used for forming the terracottas was prepared with a clay of quite similar composition, but has been diluted by 17% compared with the Mycenaean paste used for the production of members of group CYP-I. Alternatively, a different clay layer, of very similar composition but with a natural dilution, was exploited. Unknown to us, a Cypriot origin of many of these terracotta pieces was suspected previously.

FIG. 3.10. Sherd of a relief amphora (sample EME-C 76), seventh or sixth century B.C., NAA group EME-G: Dorian, probably local Knidian, origin.

FIG. 3.11. Terracotta showing left half of a human head (sample EME-C 20), 600–580 B.C., NAA group EME-A: imported from Cyprus.

For a few sherds, the location of the manufacturing workshop could be determined. Four samples, all Ionian jugs, have been imported from Miletus, three have the well known composition A of the Kalabaktepe workshops and one has a different pattern also assignable to Miletus and called D [3.22]. An example of such an imported jug with composition A is shown in Fig. 3.12. Another Ionian jug has composition EME-B and is, therefore, presumably a local imitation. Two fragments of dinoi come from Attica; they have the composition KroQ known from Mycenaean material from the Acropolis in Athens [3.29]. A fragment of one of the Attic dinoi is shown in Fig. 3.13. A more detailed description of these results can be found in Ref. [3.24].

FIG. 3.12. Fragments of an Ionian jug (sample EME-C 115), 625–600 B.C., NAA group A: imported from the Kalabaktepe workshops at Miletus.

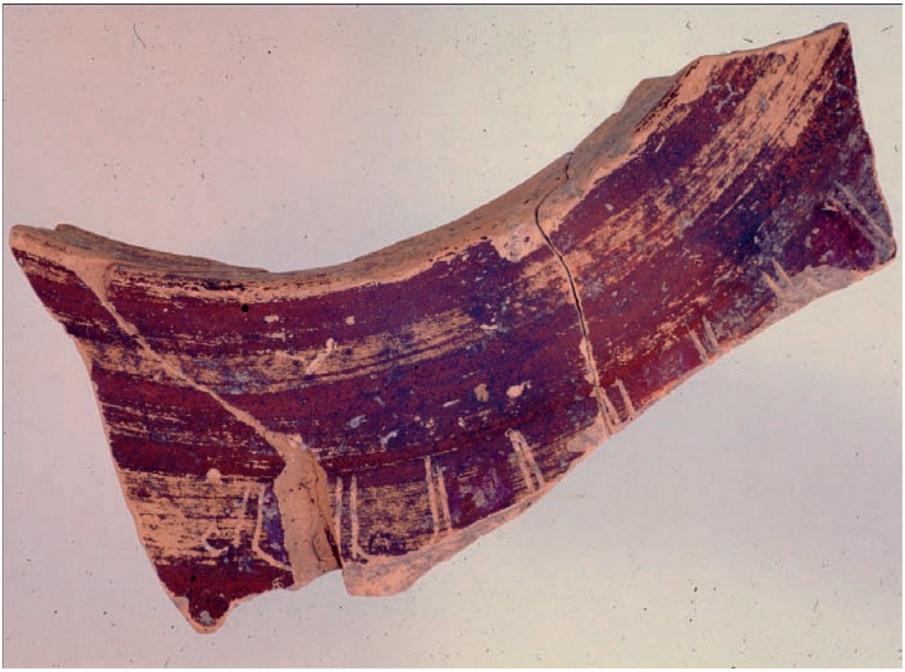

FIG. 3.13. Fragment of a dinos (sample EMEC 40), 575–525 B.C., NAA group KroQ: imported from Attica.

The provenance of all these pieces, determined by NAA, and the identification of the presumably locally made wares and imitations will help archaeologists to classify the large number of sherds not subjected to a chemical analysis. Neutron activation analysis was able to distinguish locally produced wares from the Knidian peninsula from imported wares, even from such distant regions as Attica or Cyprus. This example of a successful application of a chemical characterization and provenance determination of pottery demonstrates the usefulness of elemental analyses for archaeological research.

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Chapter 4

DATING OF ARTEFACTS

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4.1. INTRODUCTION

Forgery or imitation of art objects and relevant raw materials dates back more than three thousand years. It occurred in virtually all ancient civilizations, and continues until the present. For example, Mesopotamian prehistoric steatite (soapstone), artfully indigo dyed, resembles the much valued lapis lazuli, and several Late Bronze Age Egyptian and Greek metal objects made of cast bronzes, such as vessels, figurines and weights, contain over 5% substitutes or impurities (Fe, Zn, Sb, silicates, etc). In addition, many Kythnian (Aegean) silver coins of the fifth and fourth centuries BC contain more than 8% lead. Roman sculptors produced copies of Greek marble sculptures, and it is not clear whether the contemporary buyers knew that the objects were not genuine. With the Renaissance came a renewed interest in Greek and Roman antiquity, including art objects. This led to the first reproduction of ancient coins.

In our own time, a large number of individuals, supported by well organized laboratories almost all over the world, are engaged with a multimillion dollar forgeries business supplying an illegal market. Almost all categories of materials, single or composite (ceramics, metals, marble and other stones, glass, faience, etc.) are used for making forgeries that imitate the corresponding genuine art objects or the cultural remains of various epochs.

Reputable archaeometric laboratories, or even individual specialists, frequently receive inquiries about the authenticity of artefacts said to be art objects or items related to cultural heritage (in most instances, skilfully produced), mainly coming from museums, art galleries, archaeological collections and individuals. The scientific approach to such cases is based on the fact that all materials, along with their constituents and impurities (naturally or intentionally added), used in the past for making pieces of art and other objects, undergo gradual alteration and weathering with the elapsing time. Several categories of such alterations are known: changes in chemical composition, radioactive decay and fission, migration of elements, deformation, depolymerization, ionization, leaching and hydrolysis.

Thus, in principle, the modern materials used in recent times to imitate past or ancient objects are not naturally ‘aged’.

Among the laboratory processes used for art authenticity detection, the science based techniques of absolute dating play a predominant role, as they are considered highly reputable. Indeed, they are efficient in many, but not all, instances, for reasons explained below. This chapter briefly deals with luminescence and radiocarbon techniques, which exploit the above mentioned natural procedures of ionization and decay, respectively, as comprising the most frequently employed approaches in authenticity detection. Both techniques are regarded here as a means of investigating counterfeits.

4.2. LUMINESCENCE METHODOLOGIES: BACKGROUND

The phrase ‘luminescence dating’ is used to cover a number of techniques which mainly refer to the phenomena of thermoluminescence (stimulated by heat) and optically stimulated luminescence (OSL: stimulated by light). Luminescence dating requires solution of the equation

$$\text{Age} = \text{ED}/\text{DR}$$

where ED (measured in grays (Gy)) refers to the absorbed radiation dose, usually referred to as equivalent dose, and DR (measured in Gy/ka) to the dose rate (often misstated as annual dose), with resulting dates in thousand years (ka) within a time span of some hundreds up to 300 000 years and more, which typically reach 5–10% of the total error.

By using a luminescence technique, related to the material to be dated and the infrastructure availability, both research and routine services are possible for pottery, bricks, porcelain, sediments, coastal sand dunes, gravel deposits, naturally occurring calcite formations, slag, mortar, burnt flint, chert and obsidian artefacts.

The use of thermoluminescence as an authenticity testing method is well established and is in practice the main method applied for heated material or, more precisely, for artefacts pyrotechnologically manufactured at temperatures above 500°C. Recently, OSL has been used for the same purpose with similar results, rendering the two techniques the most extensively and routinely used techniques by both government and private researchers.

Both thermoluminescence and OSL dating methods have played a major role in the establishment of chronologies in archaeology, particularly in the pre-radiocarbon time range. Thermoluminescence and OSL methods are also referred, together with the electron spin resonance method, as trapped charge techniques and are based on the same physical principles; namely, the time dependent accumulation of electrons and holes in the lattice of certain minerals and other solid state phases.

The minerals are acting as natural radiation dosimeters: when a mineral is formed or reset, all electrons are in the ground state (valence band). Naturally occurring radioactive isotopes from the uranium and thorium series, ^{40}K and cosmic irradiation emit a variety of rays which ionize atoms. Negatively charged electrons are knocked off atoms in the valence band and transferred to a higher energy state (conduction band, Fig. 4.1); positively charged holes remain near the valence band. After a short time of diffusion most electrons recombine with holes, thus returning the mineral back to its original state. However, all natural minerals contain defect sites (e.g. lattice defects and interstitial atoms) at which electrons and holes can be trapped. For the measurement of a luminescence signal, the trapped electrons have to be either thermally (by heating) or optically (by light exposure) activated. This activates the electrons in those traps that are light sensitive, and while returning to the conduction band a certain number — being material dependent — will recombine with the holes. If such holes are luminescence centres, light emission (luminescence) is observed and recorded either as glow curves in thermoluminescence or shine-down curves in OSL. The above described energy model is rather simplified, since more and usually competitive processes occur during luminescence readings. For a detailed presentation, McKeever [4.1] and McKeever and Chen [4.2] should be addressed.

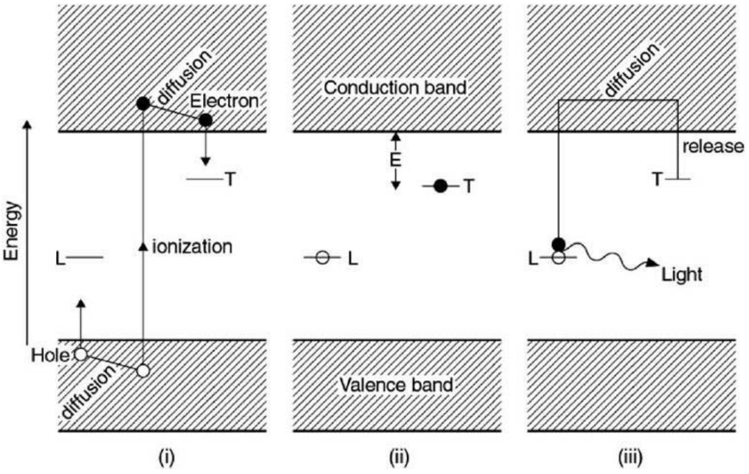

FIG. 4.1. Schematic diagram of the luminescence energy levels and main processes involved (after Aitken [4.3]), where E is the energy gap, T is an electron trap and L is a luminescence centre: (i) ionization of electrons, (ii) storage of trapped electron population, (iii) thermal or optical stimulation releases the trapped population with subsequent emission of light during recombination of electrons and luminescence centres or holes.

Figure 4.2 shows a photograph and a set-up of laboratory equipment used for thermoluminescence and OSL measurements. A mineral component of the sample is deposited on a disc, which is placed on a heater for thermoluminescence measurement. The transmitted photons are converted into electric pulses by use of a photomultiplier. The light emission versus the heating temperature is then plotted, providing the glow curve. The configuration for OSL measurements is very similar. Light in a narrow frequency range (blue or green light for measuring quartz, infrared for measuring feldspars) is focused on to the sample. The colour filters in front of the photomultiplier are used to eliminate quantitatively the light emitted from the light source; in OSL measurements the emission is plotted against the time elapsed after the light source was switched on, resulting in the shine-down curve. In most cases, the light emission for dating lies in the ultraviolet range, but other colours have also been investigated [4.4]. For more details on the instrumentation used in luminescence dating, see also Bøtter-Jensen et al. [4.5]. A series of luminescence dating applications (some of them innovative) is mentioned below, with particular interest for authenticity studies, by excluding cases not falling into this field (e.g. sediments, beach rocks, aeolianites, volcanic material, tsunamis and fault planes).

4.2.1. Dating applications

4.2.1.1. Pottery

Under the broad sense of pottery we include a wide total of artefacts and objects including end products such as vases, bricks, tiles, porcelain, terracotta and so forth, manufactured by humans using clay (of various types) as the main raw material and intentionally fired in a ceramic kiln at temperatures of at least 500°C and higher (up to about 1150°C), thus having undergone physicochemical alterations of the initial clay components and their admixtures/additives, towards creation of ceramic phases. Luminescence dating was first practiced on archaeological pottery. In recent years, however, authenticity tests on pottery items, by employing luminescence techniques, have comprised by far the main percentage of the counterfeiting avocation in reputable laboratories. Even although thermoluminescence on pottery is provided worldwide on a routine basis, possible implications regarding high temperature fired pottery, where potassium leaches, are investigated [4.6] for additional insight, in order to overcome potential age overestimation [4.7] and other deficiencies.

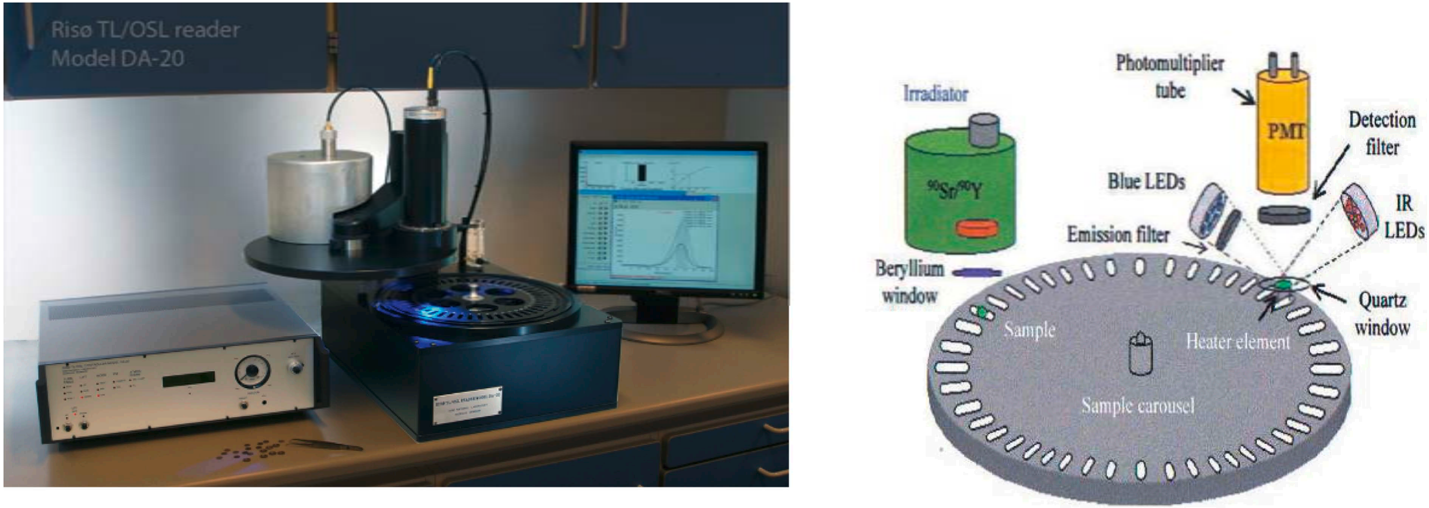

FIG. 4.2. Photograph and drawing of the recent Risø thermoluminescence/OSL reader (courtesy of L. Bøtter-Jensen). The set-up is equipped with a beta $^{90}Sr/^{90}Y$ source for artificial irradiation of the samples automatically controlled, enabling measurements of both thermoluminescence and OSL for up to 48 sample aliquots.

4.2.1.2. Burnt flint

Thermoluminescence dating of burnt flint/chert artefacts is now one of the main chronological applications, especially in prehistoric archaeological contexts, covering the time span of the controlled use of fire by humans. Thermoluminescence dating of burnt flint artefacts from the Near East in the Lower and Middle Palaeolithic period is widely used as a reference in debates on the evolution of Palaeolithic industries and on the origin of modern humans and their relationship to Neanderthals [4.8]. A detailed thermoluminescence dating study by Valladas et al. [4.9], on burned flints from the lowest Middle Palaeolithic stratigraphic unit of the Theopetra cave at Thessaly (Greece), verified that these layers are much older than previously postulated on the basis of earlier radiocarbon dating and also that Theopetra contains the oldest, so far dated, lithic artefact deposits of the Greek Middle Palaeolithic period.

4.2.1.3. Slags, pyrometallurgical remains

Ancient slag heaps present a valuable source for the technological and archaeological study of early metal production processes. Crucial to the understanding of these sites is their dating, often complicated by the rarity of diagnostic pottery fragments which necessitate the use of appropriate scientific techniques. Thermoluminescence has a great potential for absolute dating of archaeometallurgical remains, including slags, kiln fragments, fired or vitrified linings of furnaces, hearths, tuyères, crucibles, etc. [4.10], owing to the fine resetting of the 'luminescence clock' caused by the temperature of the smelting process. Direct dating of slag by means of luminescence has proved problematic in the past either with thermoluminescence [4.11] or with OSL [4.12] protocols, mainly due to the complex composition of the material and inaccuracies in microdosimetry calculations. Zacharias and co-workers [4.13, 4.14] reported thermoluminescence dating of archaeometallurgical kiln wall fragments from two Cycladic islands (Kythnos and Seriphos). Thermoluminescence dating was applied on selective layers recovered from the fragments, indicating that the metallurgical activities for both islands took place broadly in the first half of the third millennium BC, which corresponds to the Early Bronze Age period in the Aegean.

4.2.1.4. Mortars

Lime mortars mixed with sand were used extensively in architectural and decorative works during the last 4000 years. The first application of quartz OSL dating extracted from mortars referred to a Byzantine church monument dated to the tenth century [4.15, 4.16]. The same principles can be applied to any cemented materials containing quartz.

4.2.1.5. Stone courses

The potential use of luminescence techniques to date the initial or reconstruction phases of stone blocks, walls, buildings and ancient temples has intrigued specialists in the field since the 1990s [4.17] and finally provided reliable conventional [4.18] or non-destructive approaches [4.19].

4.2.1.6. Rock painting

Here, luminescence contributes to the efforts of dating rock art since this stands as an important behavioural hallmark of modern humans. The method uses quartz grains removed from fossil mud-wasp nests underlying the paintings [4.20, 4.21].

4.2.2. Techniques used for equivalent dose estimation

Since the luminescence signal should be reliable, the following properties have to be provided:

(a) When the sample is reset it may contain an initial portion; which can be either experimentally determined or assumed to be zero.
(b) The signal intensity grows linearly versus the dose received.
(c) The number of traps is constant or changes in a predictable manner.
(d) Recrystallization and crystal growth of phase transitions must not have occurred.
(e) Anomalous fading should not be present or accurate estimation should be possible.
(f) The signal is not influenced by sample preparation (triboluminescence, exposure to laboratory light, etc.).

There are several techniques for the determination of the equivalent dose (ED) value. These are mainly separated into two groups: that of fine-grain polymineral TL ones and that of quartz or feldspar coarse-grain OSL techniques.

4.2.3. Thermoluminescence techniques

The oldest thermoluminescence technique developed solely for fast ED estimation and almost exclusively used for authenticity testing is the pre-dose technique [4.22]. It is based on monitoring the sensitivity of the 110°C quartz peak which — due to saturation — limits the technique to about 1000–2000 years. This peak has a lifetime of one to two hours at room temperature and thus is not present during recording the natural thermoluminescence signal. However, due to its high sensitivity, irradiation even with very low doses (0.01–0.1 Gy) is adequate to activate this peak producing a recordable thermoluminescence signal.

The relationship for ED estimation in the pre-dose technique is given as follows:

$$\mathrm{ED} = \frac{S_{\mathrm{N}} - S_{\mathrm{o}}}{(S_{\mathrm{N}} + S_{\beta}) - S'_{\mathrm{N}}} \beta$$

where S_{o} is the natural intensity of the 110°C peak, S_{N} the intensity after an irradiation measurement cycle using a β dose and S'_{N} the signal recorded without irradiation prior to measurement.

The additive dose method is most widely used: after measuring the natural dose, several aliquots made from the same sample are irradiated with known elevating doses, thus generating more trapped electrons and increasing the thermally activated signal. Finally, the signal growth is plotted against the received laboratory dose and these data points are used to extrapolate to the initial signal yielding the ED value. A modified additive dose method is called the foil technique [4.23] (Fig. 4.3), which produces a normalized growth curve. Each point corresponds to the ratio of the thermoluminescence intensity of the first thermoluminescence measurement to the intensity of the same reference dose for every aliquot.

The regeneration technique is an alternative for ED estimation. First, the natural signal is measured and the subsequent aliquots are reset. These aliquots after external irradiation are the projection of the natural signal on to the regenerated growth curve and yield ED. This method has the advantage of creating smaller errors, since each point is measured in better detail and, furthermore, the final estimation is less dependent on the mathematical model used for the fitting of the data points.

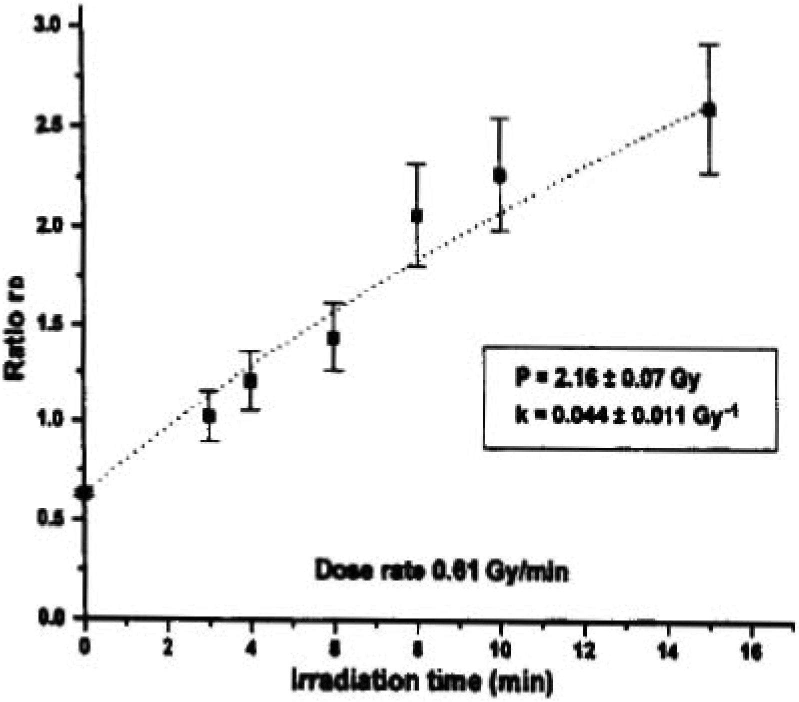

FIG. 4.3. Normalized growth curve for ED estimation using the foil technique applied on quartz samples extracted from an archaeological brick fragment.

A thermoluminescence based regeneration technique [4.24] (Fig. 4.4(a)), named SATL, using a single aliquot for ED estimation, following repeated cycles of irradiation and measurement for monitoring sensitivity changes. Although, in practice, a number (three to five) of samples have to be used for a reliable ED estimation, the technique is extremely useful when sample availability is restricted, for example, dating of small pottery fragments, or in cases of authenticity testing. In constructing the growth curve (Fig. 4.4(a)), it can be seen that the level of the thermoluminescence intensity increases with increasing measurement cycle number and eventually saturates; the resulting ED is estimated using an exponential equation in the following form:

$$T = A + B[1 - \exp(-CX)]$$

where T is the ED value and the A, B and C parameters are obtained using a computer fitting programme.

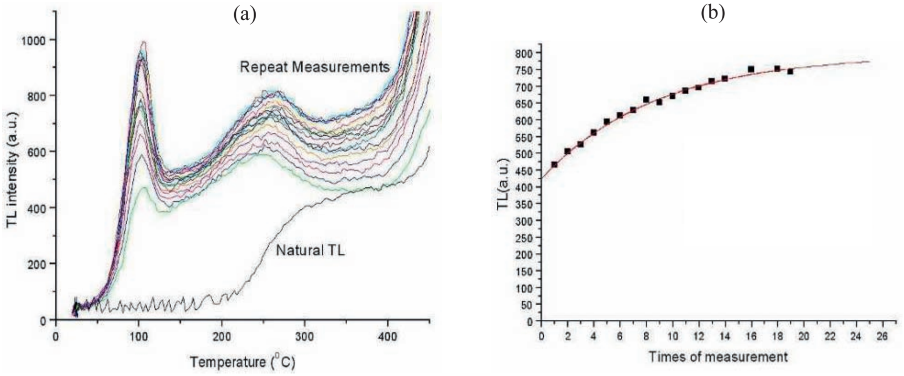

FIG. 4.4. Natural and repeated measurements of the same aliquot using the same laboratory dose in (a) the SATL technique and (b) the thermoluminescence growth curve.

4.2.4. OSL techniques

The single aliquot regeneration (SAR) [4.25] method is the most frequently applied in luminescence dating since the SAR protocol carries all measurements out on the same aliquot. First, the natural intensity is measured and then the sample is irradiated with higher doses. Sensitivity changes are monitored and corrected for by giving the sample a reference dose and measuring its response to this. The procedure followed in the SAR technique is demonstrated in Fig. 4.5 using an aliquot made of pure quartz grains.

The recently achieved infrastructural innovation by Demuro and co-workers of using single grain, single aliquot, protocols [4.26] allows independent measurements of a number of aliquots from the same source.

As a strong benefit of all SAR protocols, statistical evaluation of large ED data sets (Fig. 4.6) collected from individual samples can be used to achieve dense dose distributions and finally obtain results with lower total errors for the ages provided.

4.2.5. Estimation of the dose rate

The dose rate (DR) can be expressed as follows:

$$\mathrm{DR} = D_{\alpha} + D_{\beta} + D_{\gamma} + D_{\mathrm{cos}}$$

where α, β and γ refer to the type of rays that add up to the total dose rate and ‘cos’ stands for the cosmic irradiation contribution.

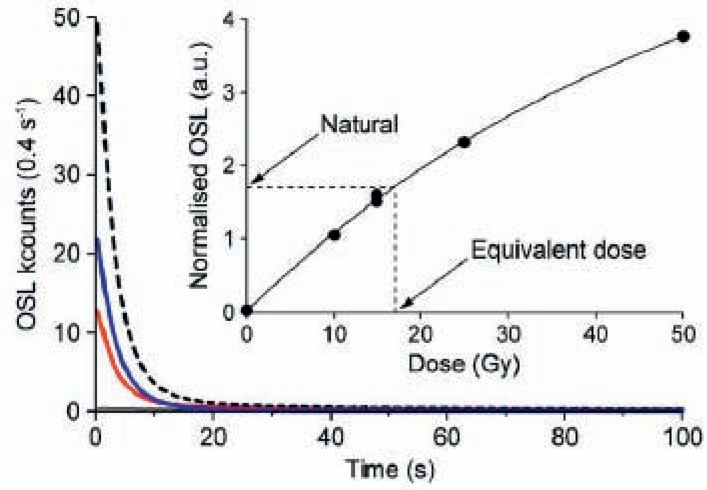

FIG. 4.5. Application of the SAR technique on a quartz-made aliquot. The blue shine-down curve shows the natural signal, the red curve the signal after irradiation with the test dose, the dotted line after irradiation with 50 Gy and the black curve following zero irradiation. The normalized growth curve of the inset shows all the points of the protocol.

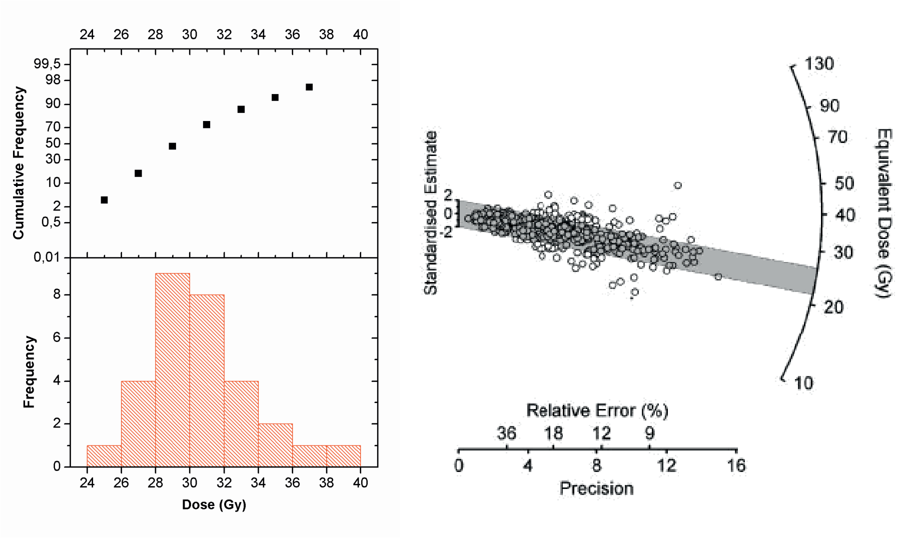

FIG. 4.6. (a) Histograms and associated probabilities [4.27] resulting from ED values measured using single aliquot SAR samples and (b) a radial plot [4.28] resulting from single grain SAR measurements.

The concentrations of the radioactive elements (U, Th and ^{40}K) in the sample are usually very different from those of its surroundings. Thus, internal and external dose rates have to be assessed independently. Furthermore, it is necessary to estimate the cosmic dose, which decreases with depth below ground and is also dependent on altitude as well as geographic latitude [4.29]. The environmental dose is best measured by employing laboratory phosphors, preferably the Al_2O_3:C type [4.30] to be buried for up to a period of three to four months, since this controls possible seasonal variations in the cosmic dose and humidity. In Fig. 4.7, the main dose rate components received by a mineral grain (quartz or feldspar) that are involved in luminescence dating are demonstrated.

4.2.6. Additional considerations for luminescence based authenticity testing

At present, faking pottery comprises a multimillion dollar business, and whilst forgeries have been around since time immemorial, as already stated, the magnitude of the deception today has reached an assumed gigantic proportion. On the other hand, authenticity testing of cultural heritage objects, using thermoluminescence and OSL protocols, is better equipped and is undertaken by laboratories specialized in archaeological material studies. As in most cases, a broader view of the object under examination is necessary; prior to application of luminescence measurements, a stylistic and technological study of the artefact is needed to address initial knowledge.

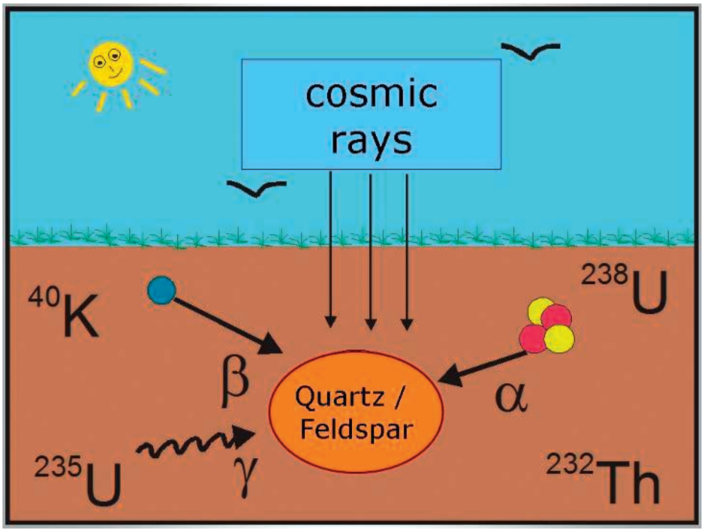

FIG. 4.7. Schematic illustration of all components involved in luminescence studies shown in the case of a quartz or feldspar grain (courtesy of G.A. Wagner).

In luminescence authenticity testing, usually the denominator of the age equation (DR) is scarcely measured due to lack of sample availability. In such cases, the use of micro-analytical techniques to provide uranium, thorium and potassium concentrations such as mass spectrometry ones (ICP or OES) or NAA is mandatory.

In general and due to the usual lack of information either about the burial place of an excavated object or about the history and the origin of an artefact, the estimation of the environmental dose is usually based on estimation and often under erroneous assumptions.

Zink and Porto [4.33], a study on the authenticity of the Tanagrae figurines of the Louvre Museum, was based on measurements of the environmental dose parameters of Boeotia, the original home of the figurines. The result of the study was that 10% of the 140 examined objects were found to be forgeries; and such a percentage is usually higher [4.34] both for private collections and for State Museum collections.

In Fig. 4.8, some of the dozens of artefacts examined per year in the Laboratory of Archaeometry at the Institute of Materials Science of the Demokritos National Centre for Scientific Research (NCSR) are presented.

In Fig. 4.9, the thermoluminescence glow curves are recorded during authenticity testing of a vase belonging to the Washington University Museum for which a typological age of 2600 years was expected (Etruscan Period). Sampling from nine points of the assemblage, including the vase and the figurines, provided almost zero age for seven of these points, while the rest, two (the snake forms), gave signals that could be attributed to the expected age. The

FIG. 4.8. Ceramic artefacts from various provenance and cultural periods: the thermoluminescence examination proved that these are not genuine archaeological objects (courtesy of Laboratory of Archaeometry, NCSR, Greece).

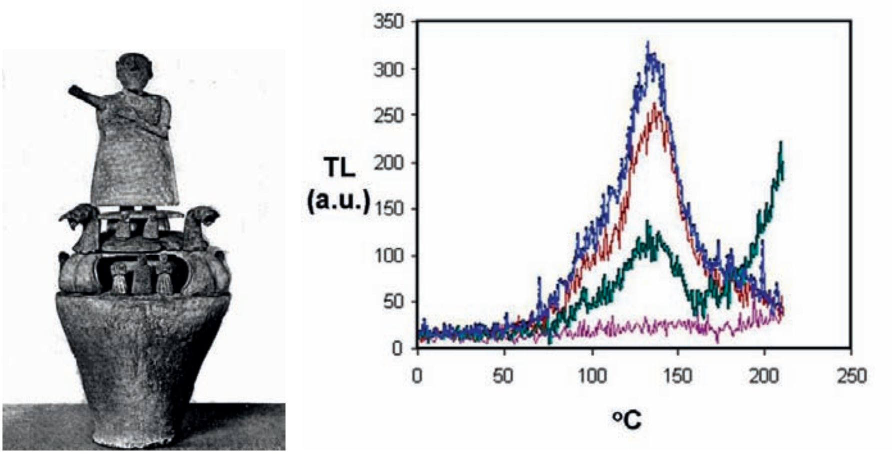

FIG. 4.9. Photograph of the Forthigham Vase (Washington University Museum); the 110°C thermoluminescence sensitivity glows are shown, monitored during the application of the pre-dose technique.

thermoluminescence examination concluded that the vase is a modern production including parts of archaeological value.

In a recent study [4.35], an unburned sherd was subjected to several heating cycles at higher temperatures; after each heating, the thermoluminescence signal was recorded. The results are shown in Fig. 4.10, where it is evident that heating at temperatures lower than 300°C for one hour does not anneal the high temperature thermoluminescence peaks. Thus, for modern replicas of archaeological objects, the combined application of moderate heating temperatures in short periods of time could produce thermoluminescence signals similar to the ‘archaeological’ ones. To avoid such implications, mineralogical testing of the temperature the artefact was exposed to, using a non-destructive technique such as scanning electron microscopy, should be applied during standard luminescence authenticity testing.

The application of luminescence techniques for dating rock art is applied in practice as an authenticity test, owing to sample restriction and lack of dosimetry information. In the pioneering approach of Roberts and co-workers [4.20], the final chronological estimation (older than 17 000 years) was based on the luminescence signals of a few quartz grains removed from a mud-wasp nest underlying the rock paintings, showing the robustness of the luminescence in both dating and authenticity testing.

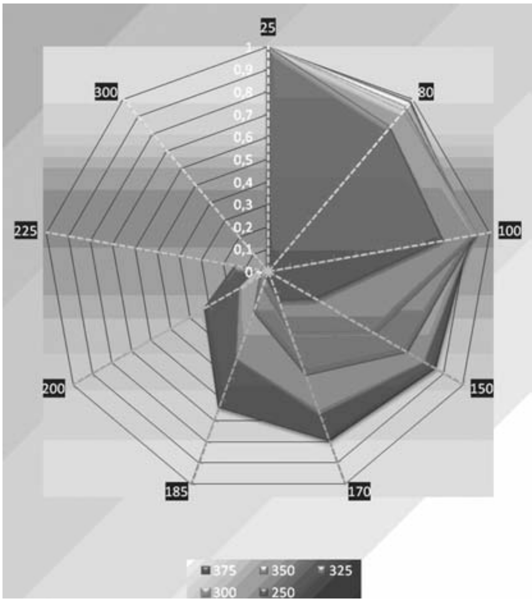

FIG. 4.10. Diagram showing the percentages of the remaining thermoluminescence signals for samples heated at 80, 100, 150, 170, 185, 200, 225 and 300°C for 1 h; the signals were measured at the glow curve areas of 250, 300, 325, 350 and 375°C.

There is one instance where a negative thermoluminescence test on a ceramic artefact could inappropriately condemn the object as being a forgery: if the ceramic has been re-fired in a kiln in modern times for some reason. This would reset its thermoluminescence clock back to zero, thus obliterating its thermoluminescence age.

In rare cases, a ^{210}Pb test might be desirable. Lead-210 is an isotope of lead with a very short half-life. If a sample of leaded bronze contains ^{210}Pb then the artefact cannot be older than, roughly, 100 years. However, if corrosion products are analysed for ^{210}Pb (by a mass spectrometer), the results might be misleading, since the corroded metallic phase can contain ^{210}Pb from the surrounding environment. Nevertheless, the absence of ^{210}Pb in a bronze does not indicate antiquity in the case when the corresponding metallic object might never have contained lead.

4.3. RADIOCARBON DATING

4.3.1. General

The ^{14}C dating technique is a scientific method for determining the age of organic carbon containing material up to about 55 000–60 000 years old. Perhaps this is the best known isotopic technique. It is routinely employed to date wood, charcoal, bone, antlers, cloth, shells, peat, carbonized seeds, etc. [4.36]. Age determination of carbonate deposits, such as calcite, dissolved carbon dioxide and carbonates in oceans, lakes and rivers, can also be performed with varying degrees of accuracy [4.37]. The technique of radiocarbon dating was developed by W.F. Libby and his colleagues in 1949 at the University of Chicago. For the pioneering invention of radiocarbon dating, Libby was honoured with the Nobel Prize in 1960.

The physical source of the ^{14}C is nitrogen gas, which makes up 78% of the earth's atmosphere. Carbon-14 occurs naturally and is formed continuously in the atmosphere. As cosmic radiation from space enters the atmosphere, neutrons are created that slow down as they collide with nitrogen atoms. These collisions result in a ^{14}C atom and a proton. The ^{14}C combines with oxygen to form CO and CO_2, which then mix with the bulk of the atmosphere containing the other stable isotopes of carbon (e.g. ^{12}C and ^{13}C). Carbon-14 behaves chemically in the same way as the other carbon isotopes. Living matter such as animals and plants constantly absorb all these forms of carbon, by food intake or photosynthesis. When living matter dies, no new carbon is added. The radioactive ^{14}C decays at a known rate back to nitrogen, and so the ratio of $^{14}C/^{12}C$ continuously decreases with time. Because the decay rate of ^{14}C is known (its half-life being 5730 years), by using appropriate liquid or gas counters (in the conventional variation) or accelerators to measure the amount remaining in a sample, it is possible to determine the time elapsed since the decease of the organism [4.38].

Modern radiocarbon laboratories report their ages in years 'before present' (BP). This refers to the number of radiocarbon years before 1950, based on the level of ^{14}C in the atmosphere equal to the 1950 level. They also report an uncertainty of 30 radiocarbon years. This statistical uncertainty is the standard deviation. Certainly, there are a few precautions or even assumptions to be made concerning this technique, which require no contamination in order to provide accurate dating estimations. In particular, special care should be taken to avoid contamination by newer carboniferous materials such as, for example, newer peaty soils mixed with old charcoal, upwelling gases containing natural carbohydrates (e.g. methane) and streams flowing over coal outcrops. In addition, large scale burning of coal and oil releases ^{14}C-free CO_2 to the atmosphere. Moreover, changes in climate in the past have caused disruptions in the carbon flow between the earth's reservoirs and the atmosphere. The ^{14}C levels have also been affected by humans: ^{14}C levels were almost doubled for a short period due to atomic bomb tests in the 1950s and 1960s. Therefore, radiocarbon dates are further calibrated for accuracy against standard methods such as dendrochronology.

The demand from archaeologists to consume virtually no material from the examined artefacts imposes application of accelerator mass spectrometry (AMS) ^{14}C dating almost exclusively. This accelerator based technique requires a very limited amount of mass (ideally 1 mg of carbon is sufficient in modern facilities), whilst a few grams of pure carbon (4–8 g) are required to perform conventional radiocarbon dating by using conventional counters. Further details on dendrochronology calibration are not mentioned here as this would extend beyond the scope of this chapter.

4.3.2. Carbon-14 dating of ancient and historical iron

Metals belong to a category of materials that still 'resist' being scientifically dated, although much relevant research effort, by employing various techniques, has been made in the last few decades. Consequently, the various types of metallic artefacts were also considered non-datable. However, it is well known that ancient steel (modern, as well) contains carbon, and thus at least carbon containing ancient and historical iron objects could in principle be datable.

In the late 1960s, van de Merwe and Stuiver at Yale University first demonstrated that it was feasible to extract the carbon contained in iron based materials and use it to establish their age by employing radiocarbon dating. They succeeded in extracting the carbon from iron by flow-through combustion in oxygen and then trapping the released CO_2 by a cryogenic arrangement. The main disadvantage of this exciting activity was the high amounts of carbon, in comparison with the overall existing carbon entrapped in the iron objects, required for the (conventional) beta counter used at that time to conduct the measurements. Hence, the technique was highly destructive, and probably not applicable for small iron samples such as figurines and daggers. Unfortunately, little carbon is required for creation of steel. Three types of carburized iron are typically known: low carbon wrought iron (containing less than 0.05% carbon), steel (with up to 2.1% carbon) and cast iron (a brittle non-hammerable material containing 2.1–5% carbon). Thus, in order to acquire 1 g of pure carbon, marginally fulfilling the beta counting requirements, one has to detach approximately 50 g of a 2% carbon containing steel object, and this is too much from an archaeological point of view.

Recent technological development, particularly the wider usage of the AMS units in research laboratories, has resulted in reducing the sample size requirement for carbon extraction and dating dramatically. The new facilities require only 1 mg instead of 1 g of extracted carbon, hence iron based artefacts can be radiocarbon dated without consuming or damaging them too much. Approximately one hundred ^{14}C datings of iron objects were published by Cook and co-workers in 2003 [4.39]. However, in order for a radiocarbon date of an iron object to be meaningful, the carbon extracted from it must originate from biomass (trees or charcoal) contemporaneous with the original manufacture. Unfortunately, this is not always the case. Theophrastus (371–287 B.C.) refers to coal (fossil fuel) used for iron working in south-west Peloponnesus (mainland Greece) already in the classical period! In addition to fossil fuels such as coal and coke, other carboniferous raw materials intentionally added to the metal such as ankerite, peat and limestone will yield chronological results much older than the real age of the examined artefacts.

Another interesting area related to the dating of carbon containing iron is the use of rust for the same purpose [4.40]. If rust could be reliably dated, many iron artefacts, several of them not retaining any metallic core, could be dated from their corrosion products, without consuming any amount of clean metal. The major issue of debate though, is whether any of the original carbon remains within the matrix of the corrosion layers, which very usually formed around the archaeological and historical iron objects or relevant pieces of art. Ongoing investigations are focused on the crystalline iron carbides (cementites and Fe_3C), appearing either as spheroidized particles or as pearlites in the iron cores, their thermodynamic history and the subsequent kinetics during the corrosion processes in various environments (ground, sea bottom, aeolian conditions, etc.). If such carbides coexist along with the commonly appearing corrosion products of iron (haematite, lepidocrocite and limonite), they could open up a large number of possibilities for dating iron artefacts without consuming any mass of the metallic core. Optical microscopy and metallography, considered highly destructive techniques, are employed in the relevant studies, albeit applied on the corrosion products, not on the real metallic substrates of the examined objects.

To summarize, all recent advances on simplification in sample preparation and reduction in sample size for AMS of iron objects containing carbon, as well as the potential use of iron rust as a viable source of material for radiocarbon dating, indicate that new achievements are expected for absolute dating of iron and, perhaps, other metallic artefacts. Even in cases when radiocarbon dating cannot determine the age of iron based materials, the application of this technique may yield valuable insight into the manufacturing practices once applied; hence, such a prospect is of paramount importance, seen from the viewpoint of authenticity studies.

4.4. CONCLUSIONS

In recent times, dating based techniques have transformed the field of ancient art authentication in a very positive and objective way. Authenticity tests on pottery items, by employing luminescence techniques, comprise by far the main percentage of the anti-counterfeiting avocation in reputable laboratories. Ongoing research aiming to minimize measurement errors and to achieve higher accuracy while using minimal mass quantities, combined with the use of thermoluminescence and OSL advanced protocols, and the exploitation of pertinent databanks, enhance the reliability of luminescence techniques and accentuate their usefulness as a powerful means in counterfeiting detection.

However, luminescence testing is unsuitable for non-ceramic artefacts, particularly for metals; the latter are traditionally known as non-datable materials. As stated above, recent developments achieved in the field of radiocarbon dating have shown that at least for some groups of non-ceramic artefacts that it was feasible to establish the age of iron based materials that contain carbon. Nevertheless, artefacts consisting partly or mainly of organic matter can be reliably investigated for authenticity by performing radiocarbon dating. In such instances, AMS ^{14}C dating has to be employed requiring only a few milligrams for the complete laboratory procedure. Here, particular attention has to be paid to ensuring that the minute samples taken for dating are not contaminated; radiocarbon dating strictly requires no contamination (a clean room environment) in order to provide accurate dating estimations.

It is known that some forgeries kept in museums or art galleries have been mistakenly labelled authentic, and contrarily, some genuine antiquities have been mistakenly condemned as forgeries, thus losing their important status. On the other hand, forgeries have been around since time immemorial, and in some exceptional instances certain forgeries of more sophisticated quality are almost impossible to distinguish from the real article without employing scientific tests. Whilst exceptionally useful and accurate in most instances, the dating based techniques employed for forgery detection, like many other scientific tests, have their own limitations, as explained. For those cases, a combination of two (or sometimes more) indicated laboratory approaches, not necessarily all falling into the dating based methods, may demonstrate beyond doubt that an artefact is definitely genuine or a forgery.

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Chapter 5

AUTHENTICITY VERIFICATION OF JEWELLERY AND COINAGES

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5.1. INTRODUCTION

Since the beginning of their existence, humankind has produced a large variety of works of art and objects — ceramic vases, metallic items and so on — according to their inspiration and skill but also according to their access to raw materials and trade routes.

Not considering paintings, the materials and objects produced by humankind in the past can be separated into two large groups. Those groups are related to the specific procedures employed for their production: the use of a thermal or of a mechanical chaîne opératoire (which corresponds to the different steps of production from the acquisition of raw material to a final object). The mechanical (cold) chaîne opératoire requires the use of tools that cut and shape a material (such as stone) to produce the necessary forms and object parts. The thermal chaîne opératoire requires the use of high temperature processes that either transform the material (such as refining metals) or produce substances by combination of different raw materials (such as glass). After these first steps of production, objects can be fabricated with those materials by again using a thermal and/or a mechanical chaîne opératoire.

The evolution of humankind's skill and innovation, the influence of other civilizations, and many other factors concerning, for example, environment, politics and social development, are inherent to the methods of fabrication of an object at a precise moment in a particular region. In addition to this, the access to certain sources of supply is sometimes a sign of power, as it indicates the control of trade routes and of particular geochemical regions. Understanding an object produced in the past is in fact a step to penetrate the secrets of the ancient craftsmen and craftswomen and to follow the history of civilizations.

The study of ancient artefacts has always been carried out by visual examination of the iconography, the style, the date and the period of production of the objects and also by comparison with well established ancient items. Carried out together with research on the ancient documents, these studies allow in some cases attesting whether an object is genuine or a fake [5.1]. However, visual observation might be inadequate to fully understand the techniques employed for production of an item and to appreciate their usage by a civilization. In most cases, this type of observation is inadequate to identify the provenance of the raw materials.

By combining art history with scientific analysis based research, fundamental information can be obtained on the production techniques of the objects and on the circulation of raw materials in the past. Since 1888, when the Chemical Laboratory of the Royal Museums, directed by Friedrich Rathgen, opened in Berlin for the study, authentication and preservation of cultural heritage, many laboratories and research centres associated with museums, universities and other public institutions have been created in many different countries. Contributing to the progress in analytical techniques applied to the field of cultural heritage, they greatly enhanced the association of art history and conservation–restoration to science based studies.

The huge variety of questions in the field of cultural heritage materials can only be tackled by a combination of visual examination of the object with scientific investigations using various types of radiation for the analysis of the constituent materials.

Scientific studies generally provide valuable information on manufacturing techniques. Usually, in the field of cultural heritage, investigations are carried out using radiography, different microscopy techniques, complemented by photography under light of different wavelengths (white, ultraviolet and infrared). On the basis of the difference in absorption of materials, X ray, gamma ray, electron and neutron radiography and tomography, invisible details of the constructions can be detected, including possible repairs and changes made by restorers or forgers. Optical electron scanning, transmission, near field, etc., microscopy techniques employ different radiations, phenomena and magnifications, supplying topographical, mechanical, structural, analytical, textural and geometrical information on the surfaces of objects and sections of samples, providing essential information on important stages of manufacture and possible alterations and restorations of objects [5.2–5.5].

Investigations are completed by analyses providing information on the elemental, structural and isotopic compositions of the materials constituting the object. These results may provide information on the nature, origin and provenance of the raw materials used in the past, as well as on some aspects of the chaîne opératoire used to manufacture the object (decoration, joining, finishing, etc.). Isotopic analysis is particularly applied to the identification of the raw materials, structural analysis to the different steps of production of an object, and elemental analysis covers all the range of questions addressed to cultural heritage.

These analytical techniques are also important in the understanding of corrosion mechanisms and identification of altered products.

Sometimes elemental, isotopic and structural analyses can be coupled to other types of methods such as those providing the date of manufacture of the object.

A large number of techniques are available to perform scientific based measurements on all types of materials [5.2]. However, use of methods to study and analyse cultural heritage objects depends critically on the constituent materials. These difficulties are due to either the use of a thermal chaîne opératoire to produce the object or to the more or less deep alteration caused by the conservation environment. In addition to these difficulties, it must still be kept in mind that precious and rare materials are recycled for reuse. The recycling processes involve a loss of information on the provenance of the raw materials, as objects from different provenances can be recycled together to produce another object. The analytical difficulties cited above are still increased for fragile, precious and rare objects, which cannot be sampled for destructive analytical techniques.

5.2. THE CASE OF PRECIOUS METALS

Silver and gold occur in rocks and ores in many ways but, unlike silver, gold can easily be found free in nature either as veins in auriferous quartz or as pellets and nuggets in alluvial deposits. Gold found free in nature is a more or less rich alloy of gold, silver and copper. Refining techniques, which have changed over time, separate the precious metals from the other elements present in the natural alloys. In the past, refining was achieved by cupellation and parting: cupellation means separating gold and silver from the base elements, whilst parting means separating gold from silver.

Precious alloys are produced by addition of other metals to gold or to silver — in general addition of copper and silver to gold to produce gold alloys and of copper to silver to produce silver alloys — according to the necessary mechanical properties (mainly hardness and tensile strength) that can also be changed by annealing, quenching and hammering. We must, however, remind the reader of the importance of the colour of alloys: the addition of copper to gold produces a reddish alloy; the addition of silver to gold produces a whitish–greenish alloy (see, e.g., Ref. [5.6]). In addition to this, the importance of the quality of the alloy (its fineness for a precious metallic alloy) should still be considered. In the case of coins, the quantity of precious metal in the alloy — silver in silver coins and gold in gold coins — is officially established by an authority, together with the weight of the coins, enabling payment by counting coins rather than by weighing.

Debasement can be carried out either by decreasing the quantity of gold or silver in the alloy or by reducing the weight of the coins. The same situation can in more recent times be found for jewellery: for example, an 18 carat gold alloy corresponds to an alloy containing 75% of gold and 25% of one or more metals whose quantities are chosen according to the required mechanical properties and aesthetic requirements of the item. In the past, the other metals were silver and copper.

The production of objects made with precious metals varies from very simple constructions to very complex constructions, the latter comprising a large number of parts joined together. Simple constructions are, for example, small cast pieces obtained by lost-wax casting followed by polishing or burnishing of the surface of coins, which are obtained by pouring the alloy into a mould or by lamination and cutting of a plaque before striking. Complex objects are produced by hammering and/or casting many different small parts that are mounted together to produce the final object. These parts can sometimes be decorated either by chasing, engraving, stamping, etc., or by addition of the same or other materials. The addition of materials can in general be attributed either to the production of polychrome objects, for example, precious stones or any other coloured material setting and niello inlaying, or to the production of low priced objects by deposition of a precious metal on the surface of a poor quality metal or alloy by silvering, gilding, depletion gilding, etc. [5.7, 5.8]. Complex objects should also be considered which are decorated by addition of small elements produced with the same alloys, such as filigree and granulation.

The fragility, rarity, value and small dimensions of objects made with silver and gold (jewellery, coins, art objects, etc.) can increase the difficulties associated with their scientific study. The study of such small objects, which sometimes consist of several tiny elements, involves the use of microanalytical techniques. Their preciousness and rarity constantly require the use of totally non-destructive techniques, but it must be kept in mind that it is the same preciousness and rarity that increases the recycling and reuse of these materials; hence, this type of transformation attains here its highest levels.

Associated with religion and power, rare and precious metals are strongly connected to the political, social and economic histories of civilizations. The study of these objects as a whole, by using science based techniques that bring together complementary information, allows tackling all the different aspects covering their production, from the exploitation of the raw material to the finishing of their surfaces, and their circulation. The identification of the decoration, joining, mounting and surface finishing techniques requires accurate observation under light of different wavelengths and different types of radiation in order to obtain information on the surface morphology and also to reveal invisible details. Much information can be recovered using techniques such as photography, macrophotography, optical microscopy, scanning electron microscopy (SEM) and X ray radiography. Low and high magnification images of the surface morphology of a gold or silver item are in general obtained by optical microscopy and by SEM. Provided an analytical system is integrated [5.9] and the object fits into the sample chamber, SEM has the advantage of combining imaging with elemental analysis. The use of high resolution surface analysis provides quantification of the tool marks on the surface of the objects related to the goldsmith decoration techniques using mechanical working (engraving, chasing, repoussé, stamping, etc.).

If many techniques of production of gold work can be described by examination, others can only be established by analytical techniques. For example, the use of fire gilding can be identified by the presence of mercury on the surface of the objects so treated. Similarly, queries related to gold provenancing and circulation can in most cases only be answered after chemical analysis. If several science based techniques are available for the study of metals, ancient gold items require the use of non-invasive techniques. Metallurgical and isotopic analyses — the first providing information on the shaping processes and the second on the provenance of gold — requiring a sample, are in many cases excluded. However, it should be mentioned that isotopic analysis was successfully applied to a few cases of silver alloys (e.g., in Ref. [5.10]) but, in the case of gold, this technique gives poor results.

Elemental analysis is the most established method for gold jewellery studies [5.11]. It can be totally non-destructive, it can give access to microanalysis, it can measure a large number of elements sometimes simultaneously even when present at low concentrations.

In spite of the poor detection limits in the case of metals, the most popular technique of elemental analysis is energy dispersive X ray fluorescence (EDXRF), a non-invasive technique using portable equipment convenient for analysis of items which cannot be moved from collections [5.12, 5.13]. With the same level of detection limits, SEM-EDX, providing imaging and elemental analysis of tiny details accurately selected on the surface of an object [5.14], is certainly the most attractive technique for the study of small gold and silver objects entering the chamber (Fig. 5.1).

For provenancing metal objects, trace element determination [5.15] frequently requires the use of large facilities: particle accelerators [5.16] and synchrotrons. Techniques such as particle induction X ray analysis (PIXE) (see, e.g., Refs [5.17, 5.18]) and synchrotron radiation X ray fluorescence analysis (SR-XRF) (see, e.g., Refs [5.5, 5.19]) based on heavy and expensive equipment are non-invasive and include microbeam and mapping facilities. In general, it is the type of incident radiation that determines the detection limits [5.20, 5.21].

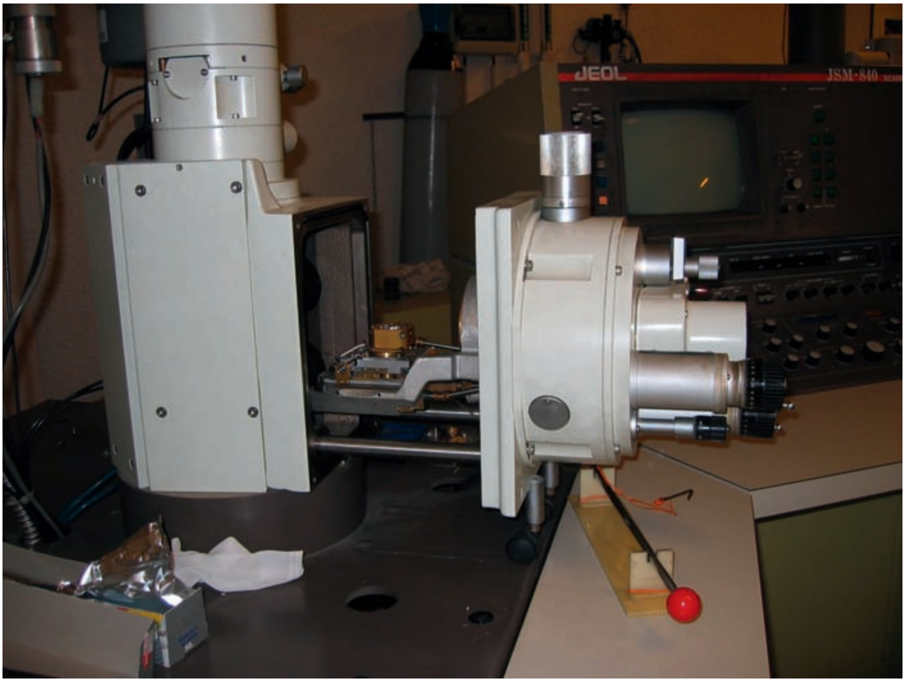


FIG. 5.1. Examination of a small gold jewellery item by SEM (© M.F. Guerra, Centre de recherche et de restauration des musées de France (C2RMF)).

In order to reach detection limits allowing the determination of ultra-trace elements, methods based on inductively coupled plasmas (ICPs) are necessary. According to the acquisition mode — solid or liquid — ICP-MS (ICP mass spectrometry) is basically destructive, but it is the only technique providing the sensitivity for trace and ultra-trace elements in gold [5.22, 5.23]. Inductively coupled plasma atomic emission spectrometry (ICP-AES), frequently applied to the elemental analysis of ancient metals, is seldom used for the study of gold items (this technique was used by Hall et al. [5.24] to study Samartian gold objects). It should be mentioned that both techniques require the removal of a sample, which is totally consumed during analysis; the sample required by ICP-AES being larger than the sample required by ICP-MS [5.23].

5.3. STUDIES ON MANUFACTURING TECHNIQUES OF JEWELLERY

In general, the main steps of production of an object are: production of the base part or small parts by casting or/and hammering, decoration,

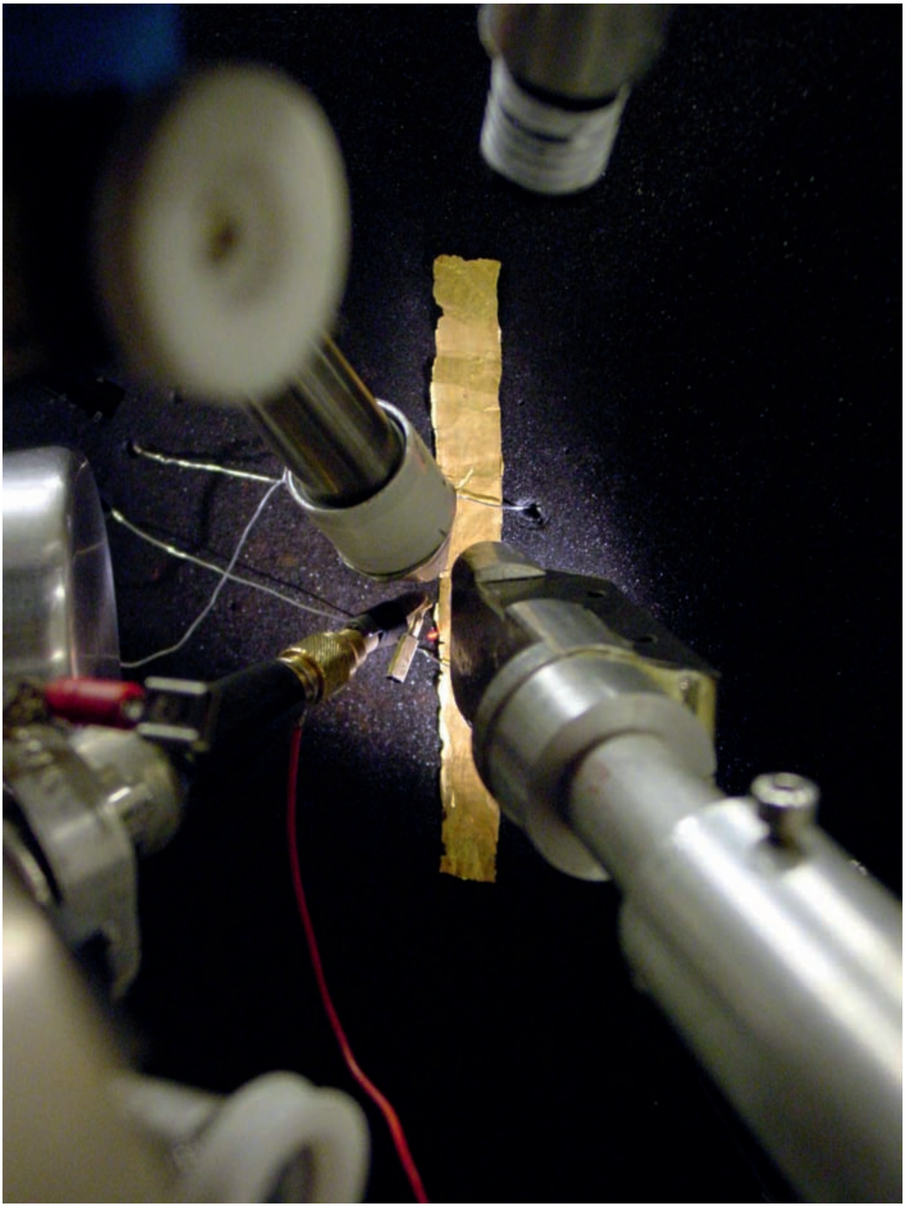


FIG. 5.2. Analysis at the AGLAE accelerator of the C2RMF (Louvre Palace, Paris) of a gold foil from the decoration of a tomb at the necropolis of Gol Mod (first century B.C. to first century A.D.) excavated by the French archaeological mission in Mongolia (© M.F. Guerra, C2RMF).

joining/mounting and finishing. For all these different steps, science based examination and analysis can contribute to the description of the goldsmith's choices [5.9, 5.25].

Low and high magnification images of the surface morphology of a gold artefact obtained by optical microscopy and by SEM reveal many details of its fabrication and conservation. This is illustrated by the study of a pair of medieval brooches produced at the end of the fifth century A.D. (Louviers necropolis, Eure, France [5.26]) by lost wax casting of a silver alloy finished by total gilding in order to make the items look like gold objects. The observation of their surface morphology and the analysis of their golden regions by SEM-EDX revealed the use of fire gilding, a gold amalgam process that became the standard gilding technique in Europe after the third century A.D. [5.27]. Used under the Romans (as referred to by Pliny) until the medieval period [5.28], it consisted in the application of either a mixture of hot mercury where gold was dissolved or of gold foils on the top of a layer of mercury [5.8]. For those brooches, we could determine the expected presence of variable amounts of mercury, as well as the application of gold foils on the silver surface. Figure 5.3 illustrates the use of these gold foils.

5.4. COMBINATION OF EXAMINATION TECHNIQUES

Additional information on the invisible parts of gold artefacts is provided by X ray radiography, which reveals the regularity of certain processes such as hammering and the internal mountings. This latter situation is illustrated in Fig. 5.4 by an X ray radiograph of a gold finger-ring found in the tomb of a male dated from the second half of the sixth century A.D. This finger-ring of simple construction consists of a hammered ribbon type hoop decorated with two spiral beaded wires and a bezel formed of a gold plaque surrounded by a spiral beaded wire. Radiography was the only technique that could entirely describe the mountings of the finger-ring by revealing the presence of an extra beaded wire for sustaining the gold bezel plaque from inside the construction.

In most situations, it is the combination of three examination techniques using incident light of different wavelengths and different types of radiation — stereomicroscopy, SEM and X ray radiography — that allows the understanding of the different steps of production of a piece of jewellery. This type of study may yet reveal if an object is genuine or just a modern construction. The study of the hinged bracelets of the Campana's collection illustrates this situation. Formerly attributed to be Etruscan and originating from Tarquinia [5.29], in 1984 the hinged bracelets were designed by J. Rudoe [5.30] as nineteenth century

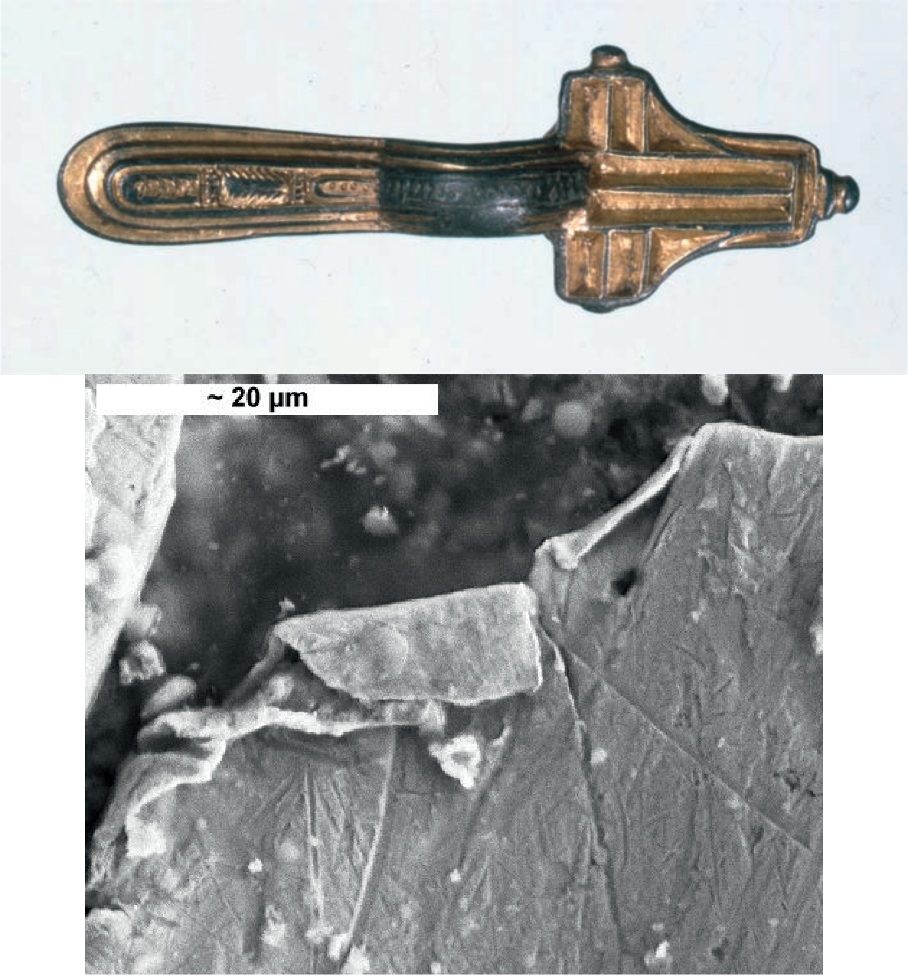


FIG. 5.3. Brooch produced at the end of the fifth century A.D. (Louviers necropolis, Eure, France (© D. Bagault, C2RMF) and details under SEM of the gold foils applied on the silver surface during fire gilding (© M.F. Guerra, C2RMF).

pastiches, composed of flattened front and rear curved panels from Etruscan ‘a bauletto’ type earrings, dated from 550 to 500 B.C., hinged together with clasps at the end. Despite the fact that they were recognized as pastiches, no evidence of their assemblage has been made known.

The X ray radiography of the hinged bracelets confirmed the assemblage of front and rear curved panels from Etruscan ‘a bauletto’ type earrings and revealed essential new details about these pieces of jewellery [5.31]: the use of ancient

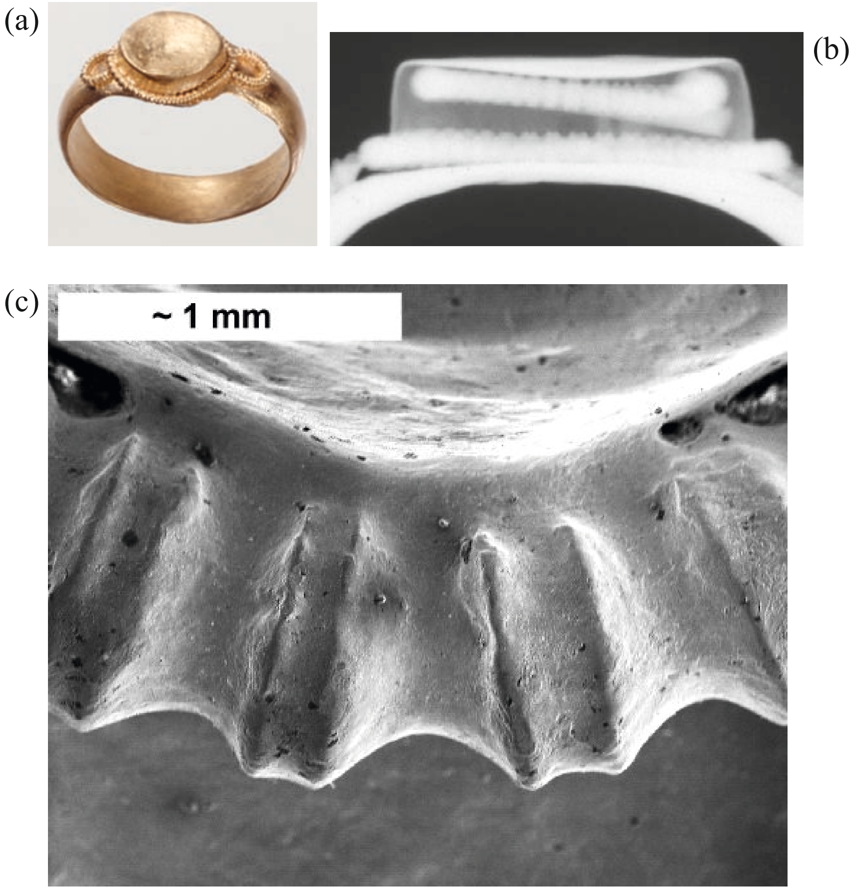


FIG. 5.4. (a) A medieval finger-ring (© D. Bagault, C2RMF); (b) an SEM image of one of the soldering points of the spiral beaded wire to the bezel gold plaque (© M.F. Guerra, C2RMF); (c) an X ray radiograph of the bezel, which discovered the internal beaded wire sustaining the bezel construction (© T. Borel, C2RMF).

gold panels of heteroclite dimensions outlined by modern motifs consisting of sequences of wire and granules. Figure 5.5 illustrates one of these plaques: a gold panel of an Etruscan ‘a bauletto’ earring outlined by a sequence of gold ‘thistles’.

Closer examination of the gold square in Fig. 5.5 under a stereomicroscope and SEM reveals the use of different techniques of wire production. Figure 5.6 illustrates the application on the central part of the bracelet square of Etruscan strip twisted wires recognized by their characteristic seams, produced by rolling a gold foil between two hard surfaces [5.14, 5.32].

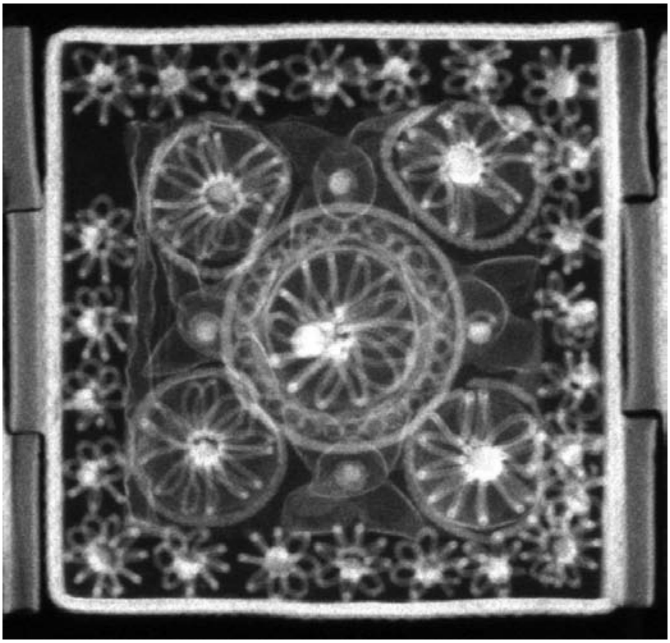


FIG. 5.5. An X ray radiograph of a gold square from one of the Etruscan hinged bracelets of the Campana's collection outlined by a sequence of gold 'thistles' (© C2RMF, T. Borel).

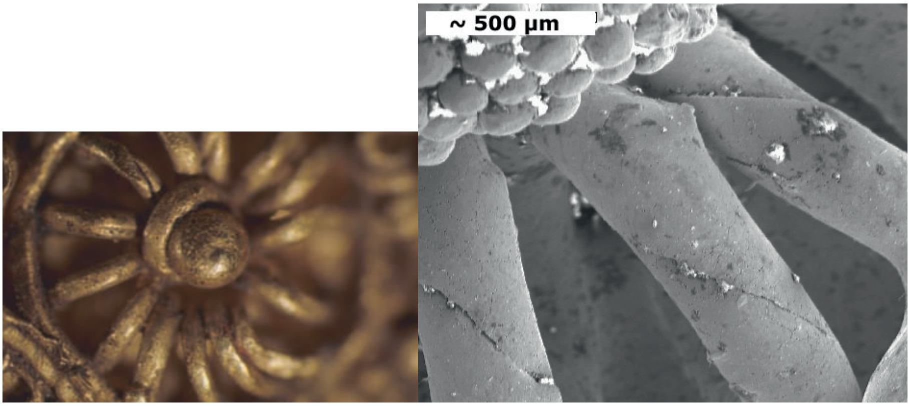


FIG. 5.6. Details under a stereomicroscope (© D. Bagault, C2RMF) and SEM (© M.F. Guerra, C2RMF) of the gold 'thistles' on an ancient central panel of a gold plaque from a hinged bracelet, showing the seam lines characteristic of Etruscan strip-twisted wires.

The bordering gold ‘thistles’ of the same gold square were obtained with modern drawn wires [5.33], recognized by their characteristic mechanical seams caused by the perforation of the drawn plate with modern tools. Figure 5.7 illustrates under the stereomicroscope and the SEM the application on the bordering sequence of the gold plaque of the bracelet square of modern drawn wires with the characteristic seams produced by drawing.

Figure 5.8 shows an X ray radiograph of another gold square from the hinged bracelets. The gold square encloses a gold panel from an Etruscan ‘a bauletto’ earring decorated with beaded wires and outlined by a sequence of modern stamped half-granules and a set of modern twisted and helicoidal wires. Under SEM, these wires show the presence of the characteristic seam lines of the modern drawn wires.

5.5. MEASUREMENT OF TOOL MARKS

The characterization of a surface can be carried out by different techniques [5.34–5.37] for different materials [5.38–5.41]. Optical microscopy, SEM and atomic force microscopy (AFM) are the most relevant for the few archaeological objects that have up to the present been studied for basic use–wear patterns, polishing techniques and engraving, and carving of gemstones and jades [5.42, 5.43].

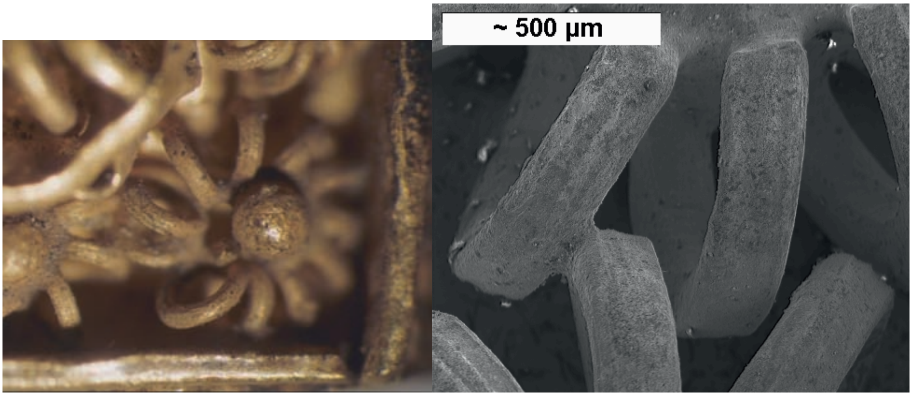


FIG. 5.7. Details under the stereomicroscope (© D. Bagault, C2RMF) and SEM (© M.F. Guerra, C2RMF) of the gold ‘thistles’ on the bordering sequence of a gold plaque from a hinged bracelet from the Campana’s collection, showing the seam lines characteristic of modern drawn wires.

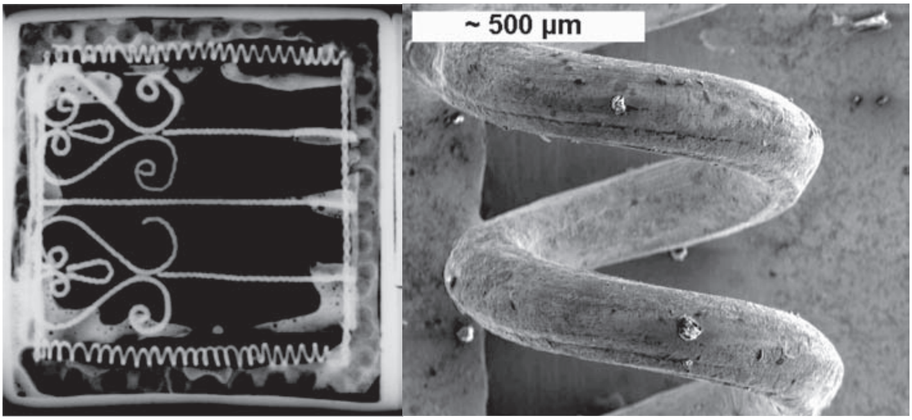


FIG. 5.8. An X ray radiograph of a gold square from the Etruscan hinged bracelets of the Campana's collection outlined by a helicoidal wire and a sequence of stamped half-granules (© C2RMF, T. Borel) and details under SEM of the seam lines characteristic of modern drawn wires (© M.F. Guerra, C2RMF).

Metals are hardly ever the subject of this kind of study and only the use–wear of dental materials and the coatings of electrical contacts are much discussed in the case of alloys with a gold base [5.44, 5.45]. Nevertheless, a few authors consider the evaluation of tool marks on jewellery by visual and microscopic observations [5.46–5.48], or the roughness and microtopography of corroded gold and silver coins [5.39] by surface quantification.

Identification of the ancient goldsmith's tools requires the ability to recognize and identify the morphology of the marks on the surface of the objects. Quantification of those marks facilitates their classification by a systematic description, rather than by individual expertise only. When non-contact analysis is required, optical techniques providing surface measurements from roughness to the digitalization of surface microtopography of small details with no previous preparation of the surface [5.37] are suitable for the study of ancient jewellery.

The chromatic coded optical principle of quasi-confocal high resolution non-contact three dimensional imaging using the appropriate optical sensor [5.49] provides an image in the colorimetric scale or in synthesis, as well as extracted profiles of a selected line. These profiles are characteristic of the technique employed, and of the tools used by the goldsmith.

Engraving, chasing, repoussé and stamping [5.50] are among the most broadly used decoration techniques of goldwork. Engraving consists of making in-depth or in-relief incisions into the metallic foil with tools chosen according to the required nature of the design and is characterized by the removal of material from the surface of the object. Designs in repoussé and chased, on the basis of the plasticity of the metal, are shaped by hammering a tool on the reverse and the obverse side of the foil, respectively. Stamping consists of the application of metallic punches to the surface of the object to form the desired design by imprinting. The pattern is repeated in-depth or in-relief.

It is worthwhile mentioning that various factors influence the character of the marks left by tools [5.51]. In the case of gold and silver artefacts, the following factors should be recalled: the angle, the force applied to the tool, the wear of the tool's edge, the possible accumulation of debris, the frequency of tool grinding and the frequency of the design starting points.

Figure 5.9 illustrates the profiles extracted of selected regions of chased and engraved lines, produced, measured with an optical sensor with a spot diameter of 3 μm, a measurement field of 0–300 μm, a working distance of 4.5 mm, a resolution of 0.01 μm and a precision of 0.1 μm. Measurements were obtained with an acquisition frequency of 300 Hz and a quantification step of 0.05 mm × 0.1 mm. Their shapes are clearly different. The asymmetric valley in the case of engraving presents an irregular surface as well as a peak on the border, corresponding to the characteristic removal of the material. In the case of chasing, a symmetric valley of regular surface and smooth border is observed.

This technique can be applied equally to the study of jewellery and coin manufacture when 'standards' of the possible decoration techniques are available or produced for comparison. We illustrate this assumption by studying the techniques used in the production of an ancient Etruscan finger-ring (from around the sixth century B.C.).

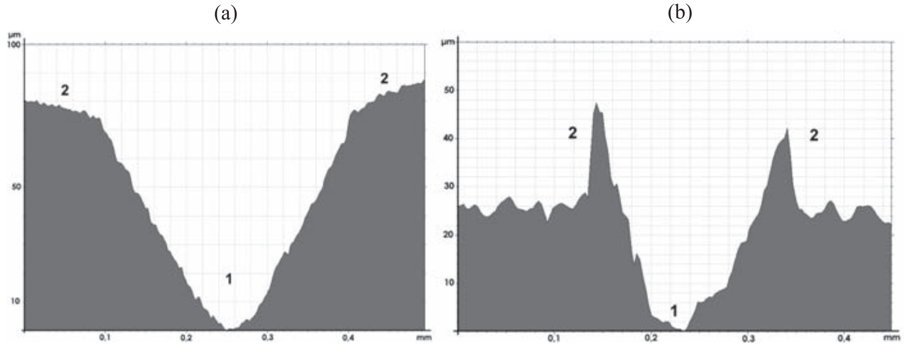


FIG. 5.9. Extracted profiles and data obtained with a 300 μm measurement field and a 300 Hz measurement frequency for: (a) a chased line for a surface of 0.7 mm × 2.8 mm area; (b) an engraved line for a surface of 0.7 mm × 4 mm area from the C2RMF workshop (Esquès et al. [5.52]).

Figure 5.10 illustrates the two dimensional representation in the colorimetric scale of the data obtained by surface analysis of a preselected region of an Etruscan cartouche finger-ring [5.53], where the design represents a chariot drawn by a winged sphinx.

The profiles extracted on two selected lines, one on the sphinx's wing and another on the wheels of the chariot, show the use of particular techniques and tools: the motif is obtained by a combination of engraving and chasing (Fig. 5.11). In fact, the gold foil constituting the top of the bezel is too thin to be decorated with the normal engraving and chasing techniques. In this case, the design is obtained with a chisel but without the use of a hammer and a burin with almost no cutting in-depth [5.52].

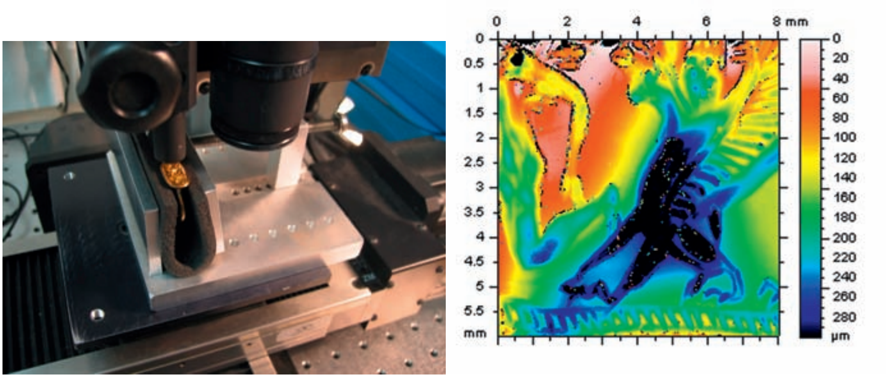
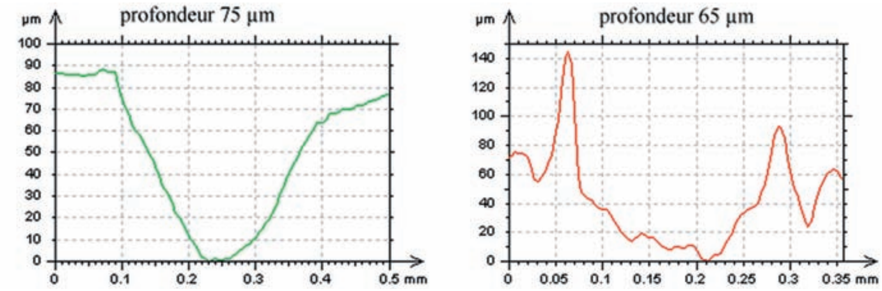


FIG. 5.10. Surface analysis of the finger-ring and a two dimensional representation in the colorimetric scale of the data obtained in the region where the motif represents the sphinx drawing a chariot (© M.F. Guerra, C2RMF).


(a)

(b)

FIG. 5.11. Extracted profiles on decoration design of the Etruscan finger-ring on: (a) the sphinx's wings and (b) the chariot wheels.

The post-processing software converting surface data into three dimensional images in the colorimetric scale or in the photosimulation give access to a clear idea about the depth of the incisions and the volume of the tool marks produced by the goldsmith. Figure 5.12 illustrates the detail of the sphinx's wings in photosimulation and the goldsmith's skill. The two dimensional colorimetric scale representation of the end parts of the wings in this same figure clearly shows the use of a triangular burin whose dimensions could be measured by using the post-processing software: 0.092 mm side; 81.5° angle.

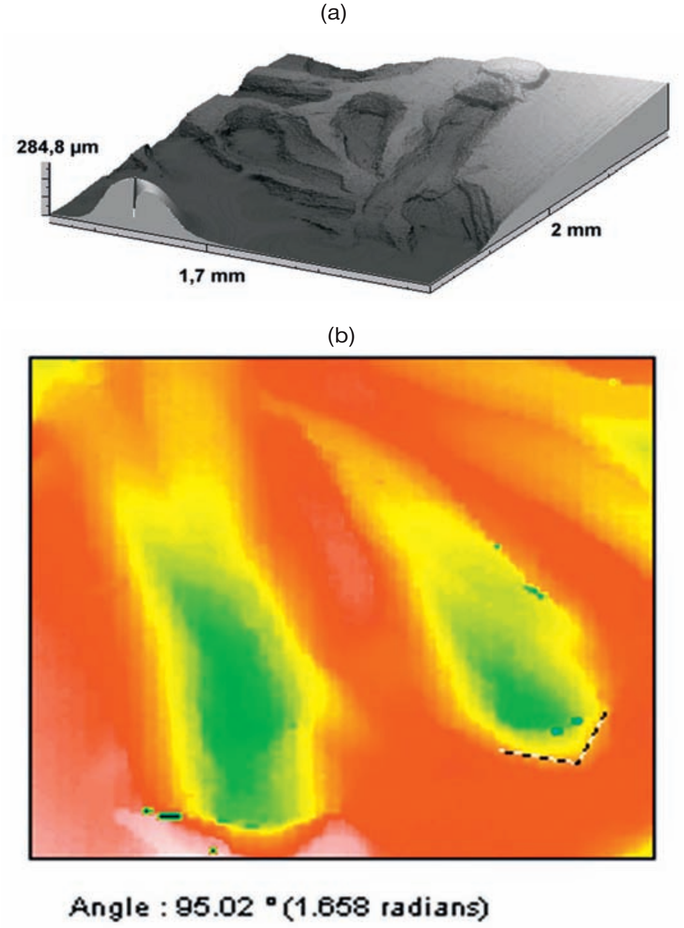


FIG. 5.12. Sphinx's wing from the Etruscan finger-ring motif: (a) a three dimensional representation in the photosimulation; (b) a two dimensional representation in the colorimetric scale (© C. Esquès, C2RMF).

5.6. PROVENANCING GOLD AND SILVER: CIRCULATION IN THE PAST

Examination and analysis reveal significant information on the life of an artefact through the study of the manufacturing techniques used in its production. However, science based techniques are of paramount importance for studies on the circulation of gold and silver in the past. These studies can identify the origin of the metal, the changes of supplies and, in particular cases, determine the localization of the exploited mines.

Three examples of provenancing studies are given in this chapter. One example considers the use of classical techniques for the identification of a change of supply. The other two examples illustrate the studies that can be achieved on the circulation of gold and silver around very large regions in the past. These two latter examples concern Europe and Latin America during the 'Age of Discovery'.

5.7. CHANGE OF GOLD SUPPLIES: A MEDIEVAL FINGER-RING

Among the 129 graves attributed to the Merovingians (Gaul, fifth to eighth centuries A.D.) found in the Louviers cemetery (Eure valley, France), one with signs of a break-in contained the remains of a male body and a gold finger-ring. The finger-ring (Fig. 5.13), attributed to the fifth century A.D., consists of a forged circular gold hoop with 'shoulders', decorated with scroll patterns filled with niello (a mixture of silver and sulphur and at times other metals), and a flat gold plaque with an engraved inscription [5.54].

The engraved plaque and the hoop, of dissimilar colours, together with their reddish joining, were analysed by SEM-EDX. The base alloys are different: 95% Au, 4% Ag and 1% Cu for the plaque and 83% Au, 14% Ag and 3% Cu for the hoop. In the gold alloy colour diagram [5.6], the finger-ring alloys correspond to:

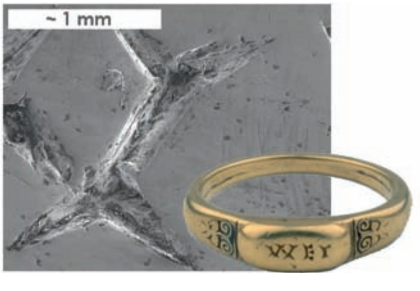


FIG. 5.13. High magnification SEM image of a platinum group element (PGE) inclusion on a finger-ring bezel under SEM (© M.F. Guerra, C2RMF).

yellow for the hoop and red-yellow for the plaque. The increase of copper and the absence of filling in the join (whose composition is on average 87% Au, 3% Ag and 10% Cu) seem to point towards the use of the copper diffusion technique. This technique allows the production of a thin joining region by applying a copper salt (such as malachite) together with an organic glue (see, for example, Ref. [5.55]).

Why would a goldsmith use two different alloys to produce one gold item? Was this finger-ring produced by two independent goldsmiths?

Observation of the finger-ring with SEM revealed the presence of platinum group element (PGE) inclusions on the plaque [5.56, 5.57] with high contents of iridium, osmium, ruthenium and platinum (Fig. 5.13 illustrates one inclusion present close to the top of letter W) and with diameters ranging from 10 µm to 150 µm [5.58]. These inclusions are characteristic of alluvial gold and can for the epoch concerned be typically found on coins struck in the Eastern Roman Empire. The absence of inclusions on the hoop indicates the use of another type of gold. Elemental compositions point out an ancient repair by addition of an engraved plaque to the ring: the hoop was made with a local gold (Gaul [5.59]) and the bezel certainly with traded gold (possibly from the Middle East).

Non-contact surface characterization based on chromatic coded confocal three dimensional imaging was carried out on the scroll patterns of the hoop and on the inscription of the plaque. The quantification of the tool marks indicates the use of dissimilar engraving tools, which could corroborate our assumption of a separated fabrication [5.60].

5.8. THE PROVENANCE AND CIRCULATION OF SILVER: THE MINES OF POTOSI

Located in ancient Peru and the present Bolivia, in the south of La Paz, the mines of Potosi were discovered in 1545 by the Spanish conqueror Francisco Pizarro. The mountain of Potosi in Cerro Rico reaches about 4000 m high, and its rich silver veins resulted in the town of Potosi growing to about 160 000 inhabitants by 1580. Believed to be induced by the discovery of this wealth and the enormous amount of money spent by Spain in the sixteenth century, a huge inflation arose in Europe [5.61]. The war in the ancient Spanish colony of Flanders and the large amount of money necessary to pay for cannons and gunpowder could have contributed to the spread of this silver in Europe [5.62].

In order to validate the arrival of the silver from Potosi in Spain and its spread through Europe, it is necessary to characterize and follow the metal from those Andean tin–silver deposits. The ruby silver deposits of Potosi are characterized by measurable quantities of quite rare elements, such as indium and germanium [5.63]. For the non-destructive determination of these elements in a silver matrix with good detection limits, a technique was developed based on the moderation of the fast neutrons produced by the nuclear reaction of a beam of 20 MeV HH^+ ions on a thick beryllium target [5.64, 5.65].

Figure 5.14 gives the concentration of indium in ppm normalized to the silver content in per cent as a function of the date of issue of a set of 'reales de a ocho' struck in the Spanish mint of Potosi and in the Spanish mints in the sixteenth century [5.66]. Indium is almost absent from the Spanish silver coins before the discovery of Potosi. However, in the period after the discovery of those silver mines, the concentration of indium in the coins issued in Spain and in Potosi under Philip II is identical. Unfortunately, before the end of the reign of Philip II, the Spanish coins do not contain their date of issue; nevertheless, one coin struck in 1597 is produced with pure Potosian silver. Hence, we are unable to determine the exact date of arrival of the silver from Potosi in Spain.

We can, however, estimate the arrival of the silver from Potosi in Spain to around 1570–1575 [5.67]. This period matches the information available from written sources: in 1570–1572 the Spanish viceroy Francisco de Toledo visited Potosi accompanied by Pedro Fernando Velasco, an expert on the mercury amalgamation technique for recovering gold and silver from ore. After 1564 the

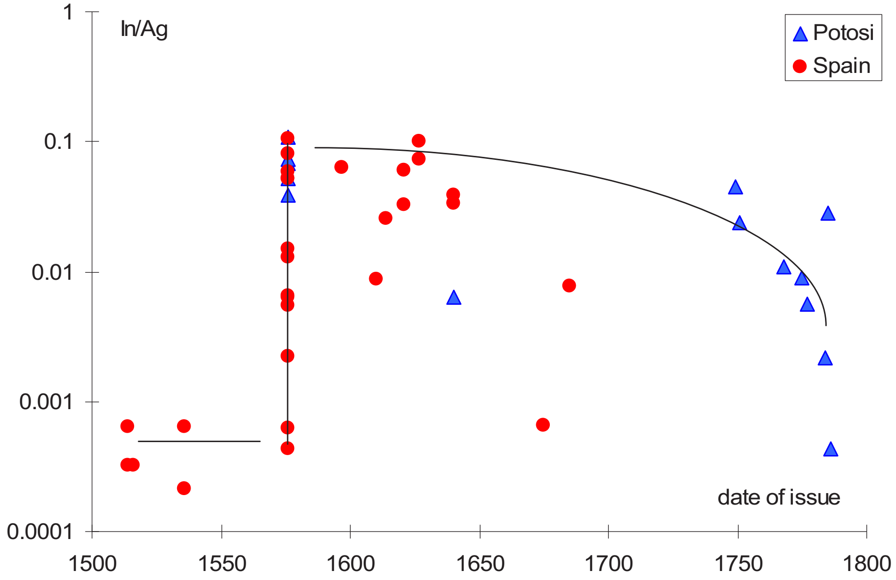


FIG. 5.14. Ratio of the concentration of indium in ppm to silver content in per cent as a function of the date of issue of a set of 'reales de a ocho' struck in Potosi and in the Spanish mints.

rich silver veins at the surface of the mountain at Potosi were exhausted. The deeper veins were poorer in silver; when treated by cupellation those veins delivered lower and lower quantities of the white metal [5.68]. With a much better yield than cupellation, the amalgamation technique allowed the mines of Potosi to produce enormous amounts of silver which flooded the Spanish mints.

In order to support the war in Flanders, a large amount of money was sent by the Spanish government to Flanders. First by sea, later through France and finally through Barcelona and Genoa, from where the money was sent to Antwerp, the silver from Potosi is supposed to have arrived in many European mints [5.62]. The coins struck in France, Italy, Barcelona and Flanders have been analysed in order to test this hypothesis [5.64, 5.65]. The results were clear. For example, in the case of French silver coins, the concentrations of indium in the alloys reached the same values as for Spanish coins. Their dates of issue specified on the coins after 1549 give the date of arrival of the silver from Potosi in France: 1575. However, if in the 1580s most of the French coins were struck with the almost pure silver of Potosi, in 1610 and then in 1627 the indium contents increased and decreased, respectively, according to the re-melts and re-issues until a final decrease in the 1640s. The quantity of silver from Potosi struck in France from 1590 to 1630 could be estimated to more than 50% of the total amount of minted metal [5.64, 5.65].

As Potosi silver arrived in huge quantities in Spain, the period of supply was short and very quickly the Andean silver was replaced by silver from another provenance. The study of the curves of production of the Mexican mines show an increase of production around 1650, at the same time as the production of Potosi decreased [5.61]. Mexican mines produced a quantity of silver that reached about three times the highest production of Potosi. Mexican silver could rapidly replace the silver from Potosi in the Spanish mints.

Figure 5.15 shows for a group of coins struck in Potosi, Mexico, Peru and Spain the concentration of gold in ppm normalized to the silver content in per cent as a function of the antimony content in ppm [5.69]. Mexican and Potosian coins form two chemical groups differentiated by their antimony and gold contents. Some of the Spanish coins appear in the group of Potosi, others belong to the group of Mexico and the rest can be found in-between these groups, including the coins struck in Lima. This clear separation into two chemical groups confirms the assumption of the replacement of the silver of Potosi by Mexican silver. The coins situated in-between these groups correspond to the transition period when silver from Potosi was re-melted together with the first Mexican silver reaching the Spanish mints for the production of new issues.

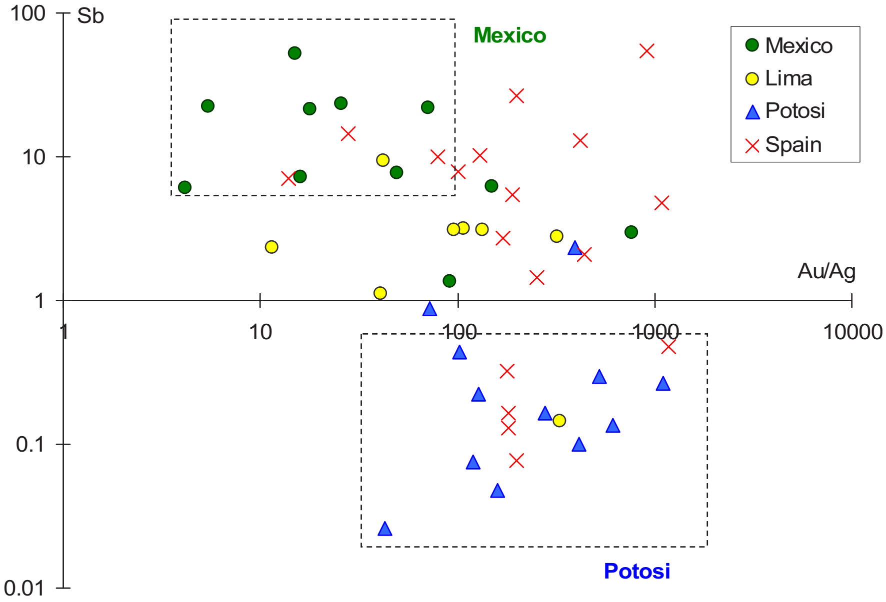


FIG. 5.15. Ratio of the concentration of gold in ppm normalized to the silver content in per cent as a function of the antimony content in ppm in a small set of coins struck in Potosi, Mexico, Peru and Spain.

5.9. THE PROVENANCE AND CIRCULATION OF GOLD: THE MINES OF MINAS GERAIS

Documents refer to the economic impact of the discovery and flow of South American precious metals in Europe after the fifteenth century: silver from Bolivia, Peru and Mexico, and gold from Colombia, Peru and Brazil. However, the provenance of the metals reaching European countries is not always very unambiguous. For example, in the case of Brazil, after the finds in 1680 of the first gold sources in the south followed by the finds in Minas Gerais in 1665, a document indicates that the first ship carrying 'Peruvian gold' reached Lisbon in 1697 [5.70].

The characterization of the main South American gold sources could elucidate this type of situation by showing whether one 'gold' corresponds to one or another source and by indicating its true economic importance. In order to check whether South American gold fingerprinting is achievable, coins issued from the seventeenth to nineteenth centuries in Mexico, Peru, Colombia and Chile were analysed together with Brazilian gold ingots. These ingots, struck

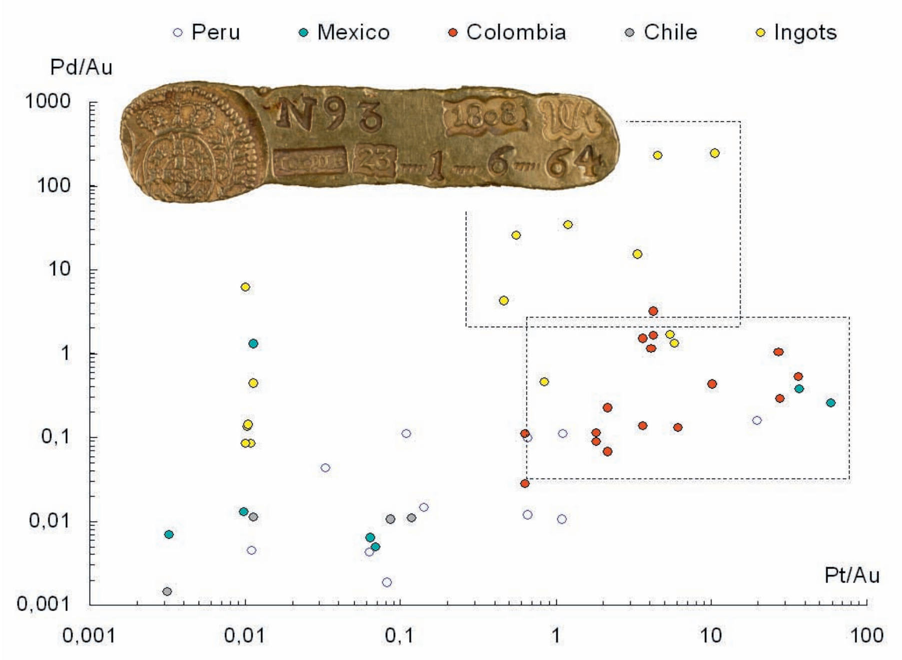


FIG. 5.16. An ingot issued in 1808 in the mint of Sabará (Minas Gerais, Brazil); platinum and palladium contents in ppm normalized to gold in per cent for Peruvian, Mexican, Colombian and Chilean gold coins and for Brazilian ingots (© MF Guerra, C2RMF).

with the mint and the minter's names together with their date of issue, were produced in the nineteenth century Portuguese royal mints in Brazil by melting gold dust and nuggets found and conveyed by gold prospectors.

The use of native alluvial platinum and gold by pre-Columbian civilizations is notorious [5.71]. The presence of palladium in Brazilian gold [5.72] and, furthermore, the association of native gold with oxygen bearing compounds of Pt–Pd–Fe for the latter, in the region of Ouro Preto [5.73] is also well established. Figure 5.16 shows the palladium and platinum concentrations in ppm normalized to the gold content in per cent measured for gold coins and ingots. As expected, different chemical groups are formed and the highest concentrations of platinum are found for Colombian gold, and the highest concentrations of palladium for Brazilian gold. In general, Peruvian gold and both Chilean and a part of Mexican gold have low contents of these two elements and fit together. It should be noted that two coins issued in Mexico and three coins issued in Peru are close to the Colombian group, illustrating the circulation of gold in the Latin American regions.

If gold circulates and is re-melted and reused in the case of South America, several chemical groups can nevertheless be defined and associated with one of

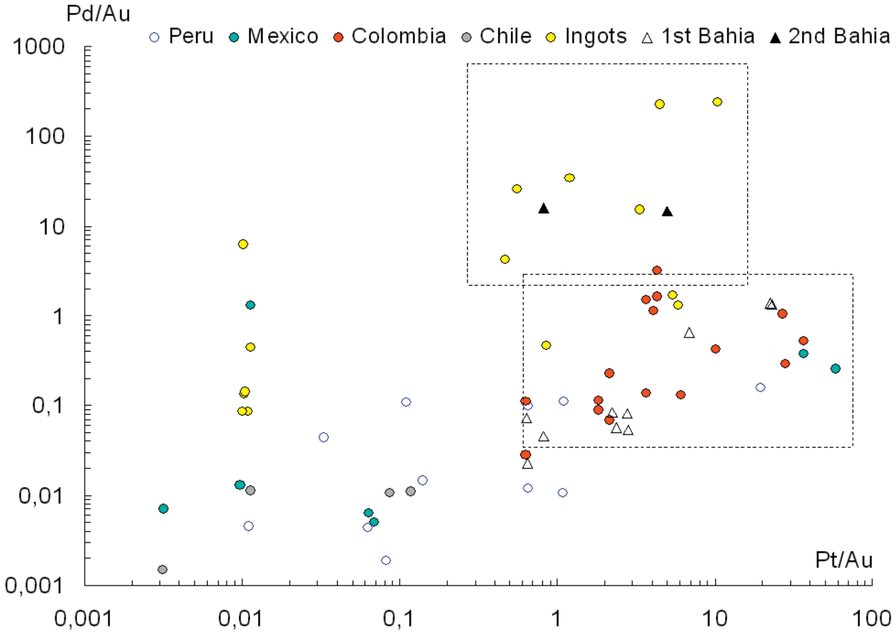


FIG. 5.17. Planinum and palladium contents (ppm) normalized to gold (%) for Peruvian, Mexican, Colombian and Chilean gold coins as well as for Brazilian ingots, together with gold coins from the first and second Bahia mints.

either of the main gold sources. These chemical groups were the basis of the studies on gold circulation in the past. When we consider that coins were struck in the Bahia mint before and after the finds of Minas Gerais, this becomes clear.

A royal decree created the first Brazilian mint in Bahia on 8 March 1694. In 1698, this mint was closed and transferred to Rio de Janeiro. Certainly related to the exhaustion of the metal stocks in the different Brazilian regions, the mint was afterwards successively closed and transferred to Pernambuco in 1700 and again to Rio de Janeiro in 1702. After 1714, many different mints opened in Brazil and a large number of gold issues started to circulate.

We analysed a few gold coins struck by the first and second Bahia mints. Figure 5.17 illustrates the palladium and platinum concentrations in ppm normalized to the gold content in per cent measured for these gold coins, together with the results previously plotted in Fig. 5.16.

Coins issued by the first Bahia mint are included in the group that fits together with the Colombian coins, whilst two coins issued by the second Bahia mint fit together with the Brazilian ingots. The first coins were struck in the seventeenth century, before the finds at Minas Gerais, when the largest amount of gold was provided by the Colombian deposits. As soon as gold was found in Brazil, in the eighteenth century, the mints started to strike local gold.

It is the previous characterization of the main gold sources in South America that shone a new light on the circulation of gold in such a vast region. The construction of 'databases' on these ancient gold sources, by analysis of the ore when possible or by analysis of carefully selected objects, is of paramount importance for provenancing studies.

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Chapter 6

NEW DEVELOPMENTS IN NEUTRON RADIOGRAPHY

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6.1. INTRODUCTION

6.1.1. Aims in archaeometry

Archaeologists search for material clues about ancient cultures, trying to answer the most frequently emerging questions:

— When was a cultural object produced?
— Where, and in which workshop, was it produced?
— Was it made of local or imported raw material?
— Is it really a significant object?

Classical archaeologists perform their research mainly on the basis of the stylistic features of artefacts. On the other hand, geologists, physicists, chemists and biologists have tried to apply the experiences of their own disciplines to cultural heritage research — already since the dawn of modern science. When investigating a valuable artistic object, the first and foremost requirement is to keep the object intact. Archaeologists and curators usually do not allow any destruction of the artefact, even if it would not be visible [6.1].

6.1.2. Neutrons in archaeometry

Fortunately, various kinds of physical processes can provide information about the material of objects, without destroying them. Neutrons are ideal for non-destructive probing of valuable objects. Since they have no charge, they can enter deep into the material irradiated and they can take part in two basic nuclear interactions. The first nuclear interaction is neutron capture, when the neutron is absorbed into the atomic nucleus. The so-called 'capture state' is an excited state of the newly formed atomic nucleus. The probability of capture (i.e. the neutron capture cross-section) depends on the neutron energy, and shows a great variation from one isotope to another. Capture of thermal or subthermal (typically MeV energy) neutrons is called thermal neutron capture, while higher energy (so-called epithermal) neutrons take part in resonance neutron capture. Following these reactions, the nuclei emit characteristic (prompt or delayed) gamma photons. On the one hand, by measuring the energies and intensities of the characteristic gamma radiation, the elemental (isotopic) composition of a sample can be determined. The analytical technique, which detects only delayed gammas, is called instrumental neutron activation analysis (INAA), while the method based on the detection of prompt and delayed gammas at the same time is called prompt gamma ray activation analysis (PGAA). On the other hand, in the neutron capture spectrum measured as a function of neutron energy by the time-of-flight (TOF) technique, resonance peaks can be considered as the fingerprints of elements. This method is called neutron resonance capture analysis (NRCA).

Besides capture reactions, thermal neutrons are also scattered on crystal plains or on individual nuclei. It is thus possible to obtain a neutron diffraction pattern of a sample, which will reveal information on the crystalline structure of a material, i.e. mineral phases, texture or porosity, similarly to X ray diffraction. The neutron scattering process is utilized by neutron diffraction (ND) or by small angle neutron scattering (SANS).

When the transmission of the impinging neutron beam is detected, a picture can be recorded of the object with clearly distinct parts of different neutron absorbing features. This is the basis of neutron tomography (NT) [6.2], which is similar to X ray tomography. In parallel with the development of large experimental facilities (research reactors and accelerators), all the above mentioned neutron based methods have already been applied to archaeometry research. Instrumental neutron activation analysis can be regarded as a routine method [6.3], while applications of NRCA and neutron diffraction in archaeometry are quite new [6.4, 6.5].

6.2. THE ‘ANCIENT CHARM’ PROJECT

The existing neutron based analytical methods, described above, are either capable of providing an average chemical (elemental or isotopic) composition of a bulk sample or of revealing a two or three dimensional image of the object with a limited resolution. This implies that a comprehensive methodology, which integrates the advantages of the previous ones, would be desirable. With this intention, European research groups have worked out a large scale scientific programme to provide a new, comprehensive neutron based imaging approach, which will be applied for the three dimensional imaging of elemental and phase compositions of objects selected as a result of a broad scope of archaeological research [6.6, 6.7]. The title of the project is ‘Ancient Charm’ and is an acronym for Analysis by Neutron resonant Capture Imaging and other Emerging Neutron Techniques: new Cultural Heritage and Archaeological Research Methods.

6.3. EXPERIMENTAL METHODS AND RESULTS

6.3.1. From prompt gamma ray activation analysis to prompt gamma ray activation imaging

Prompt gamma ray activation analysis has been applied in archaeometry research since 1997 at the Institute of Isotopes, Budapest. The method has been successfully applied to provenance studies of prehistoric stone tools [6.8, 6.9], and for the search for the raw materials used in Neolithic and pre-Hispanic pottery [6.10, 6.10]. We have also characterized baroque glass objects [6.11] and various metals [6.12]. In archaeometry research, the absolutely non-destructive feature is highly emphasized. After a few days of decay there is practically no residual radioactivity, and there is no visible damage to the object. At an early stage, we had a thermal beam of 2.5×10^6 $\text{n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ at the Budapest Research Reactor (BRR). Following the setting up of the Cold Neutron Source in 2000, we utilized a cold neutron beam of 5×10^7 $\text{n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ equivalent thermal flux [6.13]. After several upgradings of the neutron guides, we have currently reached an intensity of 1.2×10^8 $\text{cm}^{-2}\cdot\text{s}^{-1}$. Recently, another European PGAA laboratory has started operations at the FRM-II Research Reactor in Garching, Germany.

Standard PGAA, which applies a beam with a cross-section of some tens or hundreds of mm^2, is definitely a bulk analysis method. Usually, the detected major and trace components — as average values — provide reliable information to characterize homogeneous objects, such as stones, glass and metals. On the other hand, archaeologists are keen on investigating numerous complex objects with many tiny details inside or on their surface. Frequent questions are the following:

- How can we ‘focus our eyes’ on such small grains?
- How can we map these details in composition with our neutron beam?
- How can we ‘look behind’ the outer layers?
- How can we analyse the inner parts of a large object?

There is an inherent feature of PGAA for analysing smaller parts of an object, i.e. to develop elemental mapping of a larger volume. If we reduce our beam to a few millimetres in diameter and, at the same time, detect the emitted gamma photons from a very narrow solid angle, we can ‘cut’ a certain part from the body of the object. Moving the object in front of the beam — practically translating vertically and horizontally with an automated system — step by step we can map a part of interest from the object (Fig. 6.1). The PGAA measurement of each section will result in one individual spectrum. In principle, from the step of collecting the required spectra, it is ‘only’ computer work — although not easy — to reconstruct the three dimensional elemental distribution inside the object. This technique is called prompt gamma activation imaging (PGAI), and the new terminology was introduced in the Ancient Charm project [6.14, 6.15].

Borrowing from medical imaging, the intersection of the collimated neutron beam and the viewing angle of a gamma detector is called the isocentre, which is a fixed point in a space and which is the source of the information. In our case, it is a small volume rather than a point; therefore, it is better to call this the isovolume. If a sample is moved, with the isovolume fixed in space, we can collect spatially well resolved analytical information by acquiring a gamma spectrum at each sample position. However, such measurements are rather time consuming, because the reduction of the beam size results in a significant decrease in count rates. The solution comes at the price of reduced spatial

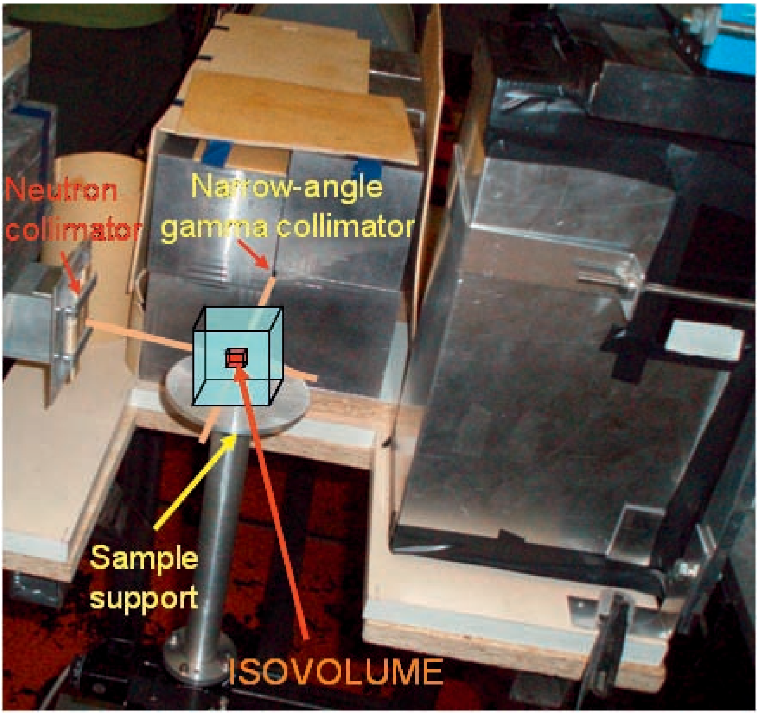
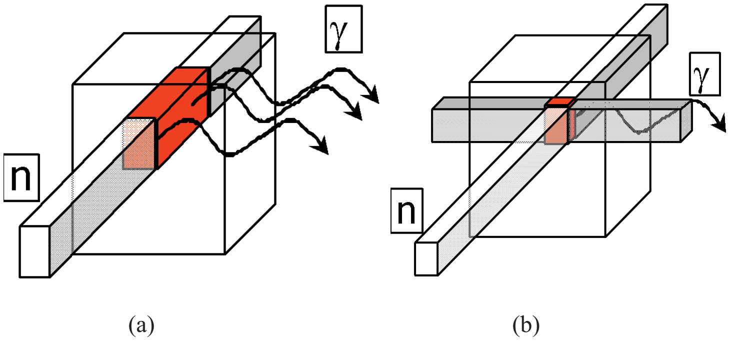


FIG. 6.1. Photograph of the PGAI/NT facility at the Budapest Research Reactor.



(a) (b)

FIG. 6.2. The sampling volume in the (a) isovolume and (b) chord geometries.

resolution: the removal of the gamma collimation results in a wide viewing angle of the detector covering the whole object, thus photons emerging from a chord shaped volume throughout the sample are detected. Therefore, the usage of this set-up is more appropriate for objects with elongated parts. Schematic drawings of the two basic measurement set-ups are shown in Fig. 6.2.

Devoting more time for experiments with successive translations and rotations of the object, the chord set-up could find its application as a base for three dimensional imaging using tomographic principles (filtered backprojection). Hence, a complete three dimensional scan of the object, in either configuration, requires a lot of beam time. It is more efficient to identify first the regions of interest using the three dimensional pattern obtained within a few hours by X ray and/or neutron tomography, and then to restrict the PGAI experiment to the determination of the elemental compositions of these regions only. This approach, called PGAI-NR/NT, considerably speeds up the investigation; it is described in the following sections.

6.3.2. Benchmark samples: 'Black boxes'

In order to establish a procedure to combine tomography, PGAI and diffraction data collected on the same archaeological object, test samples with varying degrees of complexity were analysed by the different methods. Two sets of sealed 'black boxes' were manufactured by the Hungarian National Museum (HNM) [6.16] and by the University of Bonn, Germany [6.17]. The contents of the boxes were constructed according to the design made by the archaeologists and conservators of the HNM, using typical materials occurring in archaeological contexts. The first set consists of ten iron cubes of 40 mm edge length (labelled as H-I to H-X, wall thickness 1 mm). The second set (labelled as D-I to D-X) comprises aluminium boxes with wall thicknesses of 1 mm and dimensions of

50 mm. The compositions of the internal parts, the filling materials, as well as the layout, were undisclosed to the experimentalists; however, the constructors documented the production carefully. The purpose of the experiments carried out at the Institute of Isotopes (IKI), Budapest, was to reveal as much information as possible about the materials inside of the nine black boxes selected for experiments applying PGAI-NR/NT. In several cases, complementary information from the other techniques was needed to find the composition of the black boxes. There were cases, however, when PGAI-NR/NT yielded the same information about the boxes as was given by another method [6.18].

6.3.3. Replicas and real objects

As the ultimate goal of the Ancient Charm project, a few valuable archaeological objects have been selected from museums to investigate. The one presented here is the Merovingian iron disc fibula (a type of dress accessory) with almandine ($(Fe, Mg, Mn)_3Al_2Si_3O_{12}$) inlays.

The original object was excavated in Kölked, Hungary, and it was dated to the second half of the sixth century A.D. It is a complex object in structure and material; therefore, it was ideal for application of the new three dimensional analytical methods that have been worked out in the project. In addition, it has high cultural heritage value; thus, only strictly non-destructive investigations are allowed to obtain archaeological information.

Preparatory to measuring valuable objects, preliminary tests were completed on copies, called replicas, of the original samples. The replicas of two archaeological pieces (one a Merovingian iron belt mount and a Merovingian disc fibula) are exact reproductions of the original, in both their material and shape.

It can be seen in the radiography images that the shades of the glass inlays and the pearl in the middle are different (Fig. 6.3), a result of the slightly different raw materials and production technologies. This feature could be suitable to

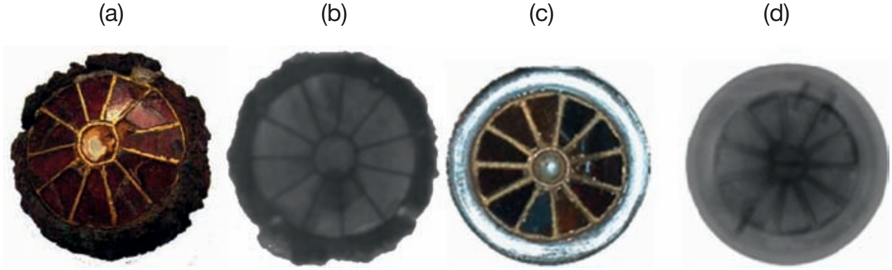


FIG. 6.3. Photographs of (a) the original disc fibula and (b) its neutron radiography image. Photographs of (c) the replica disc fibula and (d) its neutron radiography image.

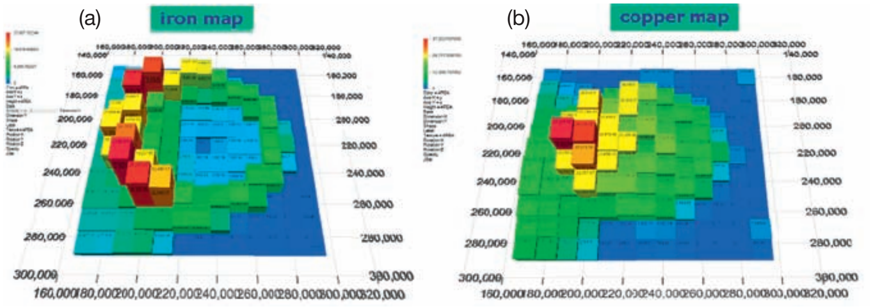


FIG. 6.4. Two dimensional element maps of (a) iron and (b) copper made on the replica disc fibula. (Raw data set; self-absorption and self-shielding are not yet corrected for.)

identify fake artefacts, even if their visual appearance perfectly resembles the original. A grid scanning of the object was performed in the chord geometry with a step size of 3 mm, resulting in 143 measurement points. In Fig. 6.4, the spatially resolved data show that the iron is concentrated at the perimeter, while the copper backing results in a more uniform distribution of the gamma ray counts. It has to be noted that the raw data presented in Fig. 6.4 are just semi-quantitative; they need to be corrected for self-absorption and self-shielding. For such a complicated object, this requires extensive Monte Carlo calculations, which are still in progress. Surprisingly, the gold content of the original fibula was found to be much higher and, accordingly, the amount of silver was lower than that expected by archaeologists. This result makes the object even more unique and more valuable [6.19].

6.4. CONCLUSIONS

It has been proved earlier that neutron based methods can be successfully used to obtain analytical information on valuable cultural heritage objects, without causing any damage to them. This feature makes them invaluable, in many cases irreplaceable in archaeometry research. Analytical signals originated from capture and diffraction reactions reveal the elemental and/or phase compositions of the objects. However, each method has its own limitations in sensitivity, penetration depth, resolution, etc.

As a conclusion of the experiments on the black boxes and replicas, different neutron based methods (PGAA, TOF-ND and NT) provide complementary information, none of them alone being sufficient. Neutron tomography produces high resolution three dimensional images that are required to survey an object for attenuation features. The contrast features in the neutron tomography images obtain a chemical and structural interpretation when information from PGAA and TOF-ND is added. PGAA can ‘see’ the elements in the bulk, which is an important analysis requirement in archaeological sciences. TOF-ND is phase sensitive and can identify structure and phases.

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Part III

CASE STUDIES

Chapter 7

CHEMICAL CHARACTERIZATION OF MARAJOARA POTTERY

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Abstract

The aim of this project was to find a signature for the archaeological Marajoara pottery. In order to achieve this goal, 330 archaeological and 36 contemporary ceramic samples were analysed using two techniques: instrumental neutron activation analysis (INAA) for elemental chemical analysis and electron spin resonance (ESR) to determine the firing temperature. The results were studied by means of principal component and discriminant analysis using the SEARCH program of H. Mommsen from the University of Bonn, Germany. The results showed the existence of two groups for the archaeological samples, indicating that different raw materials were used in the process of manufacturing these prehistoric artefacts. The same was true for the contemporary samples, which were produced from different clay sources than the archaeological ones, as was expected. The effect of clay temper on the concentration data was studied by means of correlation coefficient and showed that the dilution effect does not exist in the ceramics. The Procrustes analysis showed that the reduction of variables is viable and the chemical elements Eu, K, Yb, Cr, Fe and Th are sufficient to find the signature for Marajoara pottery. The ESR studies showed that there is no difference in the firing temperature between the archaeological and the contemporary Marajoara ceramics. This project was carried out in collaboration with the Museu de Arquelogia e Etnologia da Universidade de São Paulo, São Paulo, Brazil, and the University of Bonn, Germany, thanks to a fellowship of the IAEA for the training on the use of the SEARCH program.

7.1. INTRODUCTION

Pottery is one of the main categories of artefacts used by archaeologists due to its high rate of preservation through time, especially in contexts where organic materials deteriorate quickly. The study of ceramics provides useful evidence for several aspects of the life of past social groups. It may answer questions on diet, technology, social organization and religious beliefs. However, the archaeologist's work is limited to some extent: identifying paste composition and the source of raw materials, as well as aspects of trade and transport, calls for an interdisciplinary approach and, especially, the help of chemical and petrographic analysis. The great number of studies using different analytical methods: instrumental neutron activation analysis (INAA), X ray fluorescence (XRF) or electron microprobe analysis, shows the range and possibilities of such an approach [7.1].

During the last decade, important work on ceramic studies worldwide, covering important topics such as ceramic production [7.2, 7.3], technological change [7.4], ceramic use and distribution [7.5] and social boundaries [7.6], have helped us to better understand ceramics in their contexts. Recent studies have also examined the widespread association of potters with ethnolinguistic units and particular religious backgrounds [7.6]. The physical properties of fired ceramic material, most broadly conceived, are those that provide evidence of manufacture and those that characterize the appearance or functional capabilities of the finished piece, and mineralogical properties or chemical composition constitute a more homogeneous set of variables than do physical properties.

The chemical properties of ceramic materials are discussed in terms of major, minor and trace elements. The chemical analysis is based on the assumption that ceramics from the same production location are chemically and mineralogically similar, while being distinguishable from ceramics from other production locations [7.7]. However, the concentration levels of a number of major elements are usually similar for different samples of clay. For this reason, it is necessary to consider the chemical composition and concentration levels of trace elements in the materials from which the pottery was manufactured [7.8].

Several analytical techniques can be used to determine trace elements; however, INAA employing gamma ray spectrometry seems to be the most suitable analytical technique for archaeological studies, because it provides a means of characterizing large numbers of cultural materials in terms of objective parameters that can be used, in turn, to determine chemical elements that have great variability in their concentration.

The aim of this project was to find a signature for archaeological Marajoara pottery. In order to achieve this object, two techniques were used: INAA, to find the chemical characteristic of the pottery, and electron spin resonance (ESR), to determine the firing temperatures. The data set obtained with the archaeological samples was compared with contemporary replicas of Marajoara pottery, to verify the authenticity of the pottery, and to avoid fraud and illegal commerce.

7.2. IMPORTANCE OF MARAJOARA POTTERY

Marajó is a 49 000 ft^2 (4552 m^2) island, which is part of an archipelago that lies at the mouth of the river Amazon. The nutrient rich, muddy, sediments carried along by this mighty river are partially deposited on the island's south-western side, where the vegetation is characterized by a luxurious forest. On the north-eastern part, a shoreline of emergence, developed in the Holocene, deposits with a much lower rate of sedimentation [7.9], is responsible for a flat grassy and shrubby savannah landscape. There, seasonal floods brought by intensive rains which characterize the wet winter of the Amazon region obligated pre-Columbian inhabitants to cope with the dramatic intercalation of flood and drought. About 1500 years before the European conquest of the continent, there emerged one of the most intriguing indigenous societies of the Americas. Their exuberant culture was characterized by the construction of huge earthen mounds up to 12 m in height and 3 ha in area, the production of elaborate ceramic vessels and other objects used in ceremonies, feasting and rituals, the participation in long distance exchange networks, as well as the development of complex techniques of landscape management (construction of dams and fish ponds).

Marajoara ceramics have been studied intensively since the nineteenth century, especially in relation to vessel function, production processes and style. During the second half of the twentieth century, scholars made a dedicated study of the society itself, focusing on issues of social organization, subsistence patterns and material culture [7.10–7.15]

Radiocarbon dates place the period of major growth and expansion of Marajoara culture between the fifth and fourteenth centuries. The Marajoara style seems to be related to different regions within the Marajoara domain, as well as to different chronological periods.

The Marajoara's ceramics belong to the Polychrome tradition, characterized by highly complex ceremonial wares in form and decoration. Decorative techniques involve painting, incision, excision and scraping. The ceramics are tempered with ground potsherds (grog), but pottery tempered with crushed ashes of a tree bark known as caraipé (*Licania scabra*) is also found. The use of caraipé as temper material was introduced in the island about A.D. 500. This material was used in the Amazon Basin towards the end of the first millennium and it is associated with other ceramic complexes of the Polychrome tradition [7.14].

The economy of the Marajoara people was based on fishing, which finished at the end of the season, when the full water level began to go down and at this time they would build dams. They used structures made from wood and vegetable fibres locked along the length of the igarapés (deep Amazon river canals within the forest) and the exits of the lakes in order to dam in the fish. The fish were imprisoned in the reservoirs, and fishing was carried out with nets or locked straw baskets. Besides the fish, they probably would consume the turtles imprisoned in the reservoir in order to consume eggs and meat. Turtle fat is known as an excellent preservative and can be used to preserve the fish and meat of other animals [7.14].

7.3. EXPERIMENT

7.3.1. Sample preparation and standard

In all, 330 ceramic samples (294 archaeological and 36 contemporary) were analysed via INAA. The ceramic powder samples were obtained by cleaning the outer surface and drilling to a depth of 2–3 mm using a tungsten carbide rotary file attached to the end of a flexible shaft, variable speed, drill. Depending on the thickness, three or five holes were drilled as deep into the core of the pottery as possible without drilling through the walls [7.16]. Finally, these materials were dried in an oven at 105°C for 24 h and stored in a desiccator.

The constituent elements in coal fly ash (NIST-SRM-1633b) were used as the standard, and IAEA-Soil-7, Trace Elements in Soil, was used as reference sample in all the analyses. These materials were dried in an oven at 105°C for 24 h and stored in a desiccator until weighing [7.17].

7.3.1.1. Description of the method

For INAA about 100 mg of ceramic samples, NIST-SRM-1633b and IAEA-Soil-7, were weighed in polyethylene bags and wrapped in aluminium foil. Groups of eight samples and one of each reference material were packed in aluminium foil and irradiated in the research reactor pool, IEA-R1m, from the IPEN-CNEN/SP laboratory at a thermal neutron flux of about 5×10^{12} $n \cdot cm^{-2} \cdot s^{-1}$ for 1 h.

Two measurement series were carried out using a germanium (hyperpure) detector, model GX 2519 from Canberra, with a resolution of 1.90 keV at the 1332.49 keV gamma peak of ^{60}Co, and a model S-100 MCA detector from Canberra with 8192 channels. Potassium, La, Lu, Na, U and Yb were measured after seven days cooling time, and Co, Cr, Cs, Eu, Fe, Sc, Ta, Tb, Th and Zn after 25–30 days. A gamma ray spectra analysis and concentration measurements were carried out using the Genie-2000 NAA processing procedure from Canberra.

Electron spin resonance is used to detect atomic level magnetic moments, which include paramagnetic ions such as the transition metal or rare earth ions, and also other electronic states with unpaired electronic spins. In this work, the firing temperature was studied by means of the changes in the ESR spectra of Fe^{3+} after the ceramic was refired at successively higher temperatures (100–850°C), and the temperatures at which major changes in peak intensities occur suggest the original firing temperature of the ceramic. The samples were carefully ground with a mortar and pestle, and the fraction between 88 and 180 μm was selected.

The ESR spectra were taken at room temperature and 77 K, below saturation, by means of a homodyne X-band VARIAN E-4 spectrometer with 100 kHz magnetic field modulation, a 20 mW microwave power source and a TE_{011} mode cavity. The modulation amplitude used was 2.5 G peak to peak and the scan speed was 4000 G in 480 s for room temperature measurements, and at 77 K it was 2.0 and 100 G in 60 s, respectively.

7.4. RESULTS AND DISCUSSION

The precision of the analytical technique in archaeometric studies using trace elements is the basic premise in this kind of study. If an element used in the data interpretation is not measured with good precision, when multivariate statistical methods are used, such as principal component analysis (PCA) or/and discriminant analysis (DA), this affects the other well measured elements and the discriminant effect tends to be reduced. In this project, the precision of the method was studied using the reference material IAEA-Soil-7. A comparison between the results obtained and the certified values was made. The precision was expressed as a relative standard deviation (RSD); the elements with RSDs of less than 10% were used in the Marajoara data interpretation [7.16].

All possible interferences potentially occurring in gamma ray spectrometry were considered and checked. A possible source of error in the determination of rare earth elements (REEs) is the presence of significant amounts of fissile nuclides (^{235}U and ^{233}U). As is well known, REE nuclides, especially among the light REE elements (lanthanum to samarium), are produced both by activation and by fission. In this work, no interferences were expected in the samples because of the very low uranium fission in the determination of lanthanum and cerium. This interference is negligible when the uranium concentration does not exceed 5 ppm [7.18]. Although cobalt and tantalum had RSDs less than 10%, these were not included in the data set because the concentration can be affected by tungsten carbide files [7.19]. The determination of zinc is not reliable as a consequence of strong gamma ray interference by ^{46}Sc. Using these criteria, the elements Cr, Cs, Eu, Fe, K, La, Lu, Na, Sc, Tb, Th, Yb and U, were used in the subsequent data analysis. None of the elements considered had missing values. In total, 330 samples were analysed.

Initially, the results were transformed to $\log_{10}$ to compensate for the large differences of magnitudes between the measured elements for the trace level and for the larger levels. The $\log_{10}$ transformation of data before a multivariate statistical method is common. One reason for this is a belief that within the manufacturing raw material, elements have a natural log–normal distribution and that normality of the data is desirable. Another reason is that a logarithmic transformation tends to stabilize the variance of the variables and would thus give them approximately equal weight in an unstandardized multivariate statistical analysis.

All individual determinations in each data set were tested for discordant results. The Mahalanobis distance, D_i, is suggested by many authors as a method for detecting outliers in multivariate data [7.20]. For each of the n samples in a p variable (element) data set, a distance value D_i was calculated. Let $\bar{x}$ be the sample mean vector and let S be the sample covariance matrix,

$$D_i = \sqrt{\left[\left(x_i - \bar{x}\right)^{\mathrm{T}} S^{-1} \left(x_i - \bar{x}\right)\right]} \qquad (7.1)$$

and

$$S = \sum_{i=1}^{n} \left(x_i - \bar{x}\right)\left(x_i - \bar{x}\right)^{\mathrm{T}} \Big/ (n-1) \qquad (7.2)$$

for $i = 1, \ldots, n$, where $x_i - \bar{x}$ is the difference vector between the measured values in one group and the mean values of the other group. Wilks [7.21, 7.22] suggested the use of

$$p(n-1)^2 F_{p,\, n-p-1} / [n(n - p - 1 + pF_{p,n-p-1,\alpha/\mathrm{n}})] \qquad (7.3)$$

to calculate the critical values for D_i when searching for a single outlier. Wilks used the so-called scatter ratios to search for outliers in multivariate normal data. To search for a single outlier, a scatter ratio R_i,

$$R_i = |A_i| / |A|$$

is calculated, where

$$A = \sum_{i=1}^{n} \left(x_i - \bar{x}\right)\left(x_i - \bar{x}\right)^{\mathrm{T}} \tag{7.4}$$

in which $|A|$ = determinant(A) and A_i is calculated as for A with observation i eliminated from the sample. The most outlying observation is the one with the smallest scatter ratio R_i, where

$$R_1 = \min\{R_i\}$$

i.e. the observation whose removal leads to the greatest reduction in $|A|$. This procedure at a confidence level of 95% was applied to the data set. The D values were calculated for all samples. When the D calculated in the sample was higher than the critical value of the sample D, it was eliminated and a new D was calculated, i.e. in the results, 11 archaeological and three contemporary samples were eliminated and were not included in the data set.

The application of statistical methods in experimental results aims at classifying and ordering objects related to each other in function, exclusively from their chemical compositions. Various multivariable statistical techniques have been used such as PCA and/or DA when compositional data are highly correlated. In the PCA technique, the transformation of the data set is based on eigenvector methods to determine the direction and magnitude of maximum variance in the data set in hyperspace. In the DA technique, the difference between two or more groups is maximized. This technique is based on the fact that the principal variance–covariance matrix is an accurate representation of the total variance and covariance.

Then, for the purpose of studying the similarities and dissimilarities between ceramics, the results were submitted for PCA and DA. The intention was to group similar samples according to their characteristics (variables). The purpose, therefore, is to consider several simultaneously related variables, all of them having equal importance at the beginning of the analysis. Another consideration is that the data must follow a normal distribution. In general, if each studied variable follows a normal distribution, the resulting distribution of the group of all the variables will also be normal.

Figures 7.1 and 7.2 show principal component 2 versus principal component 1 and discriminant function 2 versus discriminant function 1, respectively, for all the ceramic samples studied. The results showed that there is 100% separation between the archaeological and contemporary ceramics, i.e. there is a clear difference in the chemical compositions of the archaeological and contemporary Marajoara ceramics.

Hypothetically speaking, temper effect could be the primary contributor to group separation. To confirm this last assumption, the data were submitted to the correlation coefficient, because negative correlations are possible if certain constituent elements present in the clay are diluted by the temper. The results do not show negative correlations, indicating that the separation between the groups is due to differences in clay selection.

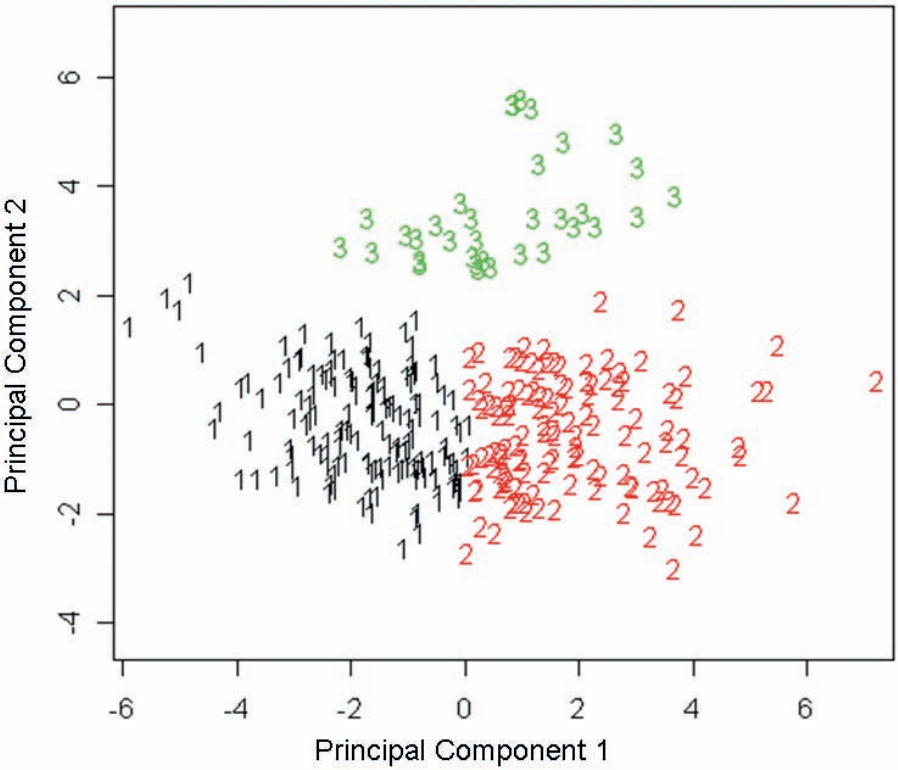

FIG. 7.1. Principal component 1 versus principal component 2 using all variables (Cr, Cs, Eu, Fe, K, La, Lu, Na, Sc, Tb, Th, Yb and U). Groups 1 and 2 are archaeological Marajoara ceramics and group 3 contemporary Marajoara ceramics.

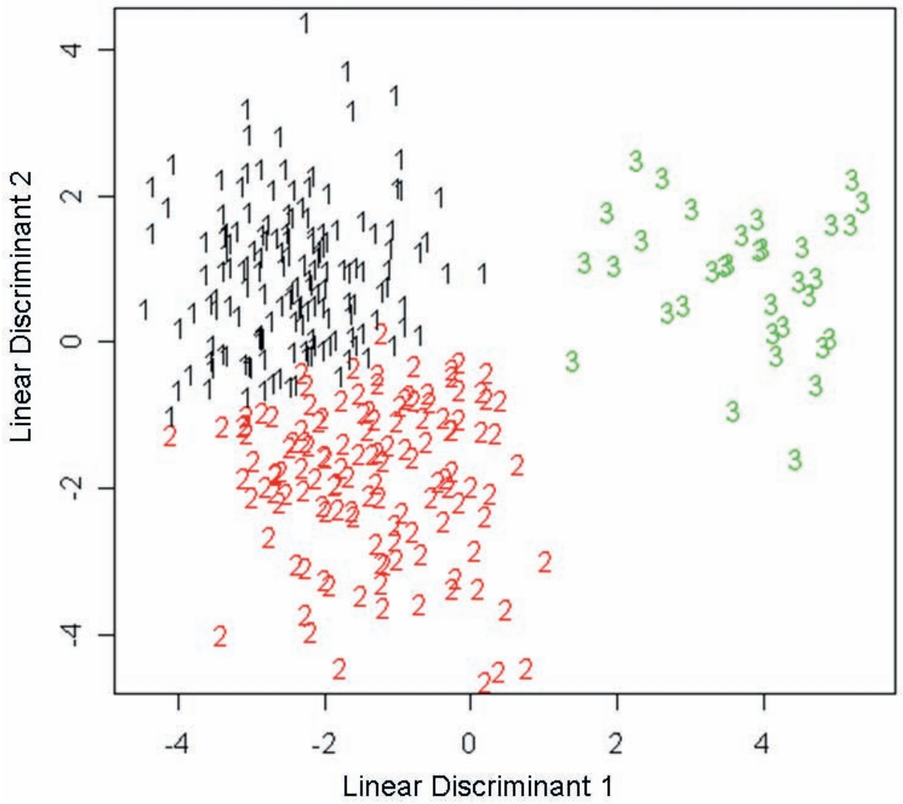

FIG. 7.2. Linear discriminant function 1 versus linear discriminant function 2 using all variables (Cr, Cs, Eu, Fe, K, La, Lu, Na, Sc, Tb, Th, Yb and U). Groups 1 and 2 are archaeological and group 3 contemporary Marajoara ceramics.

7.4.1. Variable selection

In general when characterizing samples by means of chemical elements for the first time, such as Marajoara ceramic samples, the analyst measures a large number of variables, many of which may not be very informative. In fact, some may even be unrelated to the issue at hand, and blur the picture instead of making it clearer. In subsequent studies, the analyst may wish to measure fewer variables for several reasons, such as to save time in cases where measurement time is important or in order to reduce cost or effort. Therefore, hopefully those variables that are most relevant will be determined without losing essential information, and the less productive information will be removed.

A procedure for the identification of redundant variables for Marajoara ceramics is presented here, as well as the selection of variable subsets preserving multivariate data structure. A Procrustes analysis was used by selecting those variables that are in some sense adequate for characterization purposes.

Procrustes analysis consists of a criterion with the following algorithm [7.23]. Assuming that a matrix **X** with p variables (elements) has been measured on each of n samples, and that the essential dimensionality of the data to be used in any comparison is k, then the PCA procedure is based on the $n \times p$ data matrix and the scores of n samples on the first k principal components are retained in the matrix **Y**, whose columns consist of the scores on the first k principal components of **X**. Then **Y** is an $n \times k$ transformed data matrix of principal component scores of the original **X** data configuration. Select q of the original p variables, with the condition $q < p$ for the selection to take place and $q \geq k$ for recovery of the real structure with the selected variables, and $n \times q$ is the matrix $\tilde{X}$ considered as a selected variable matrix that retains only q selected variables. Assuming that $\tilde{Z}$ is the $n \times k$ matrix of principal component scores of these reduced data, this is the best k dimensional approximation to the q dimensional configuration defined by the data subset. If the real data dimension is really k, then **Y** can be seen as the real configuration, while $\tilde{Z}$ is the corresponding approximate configuration based only on q variables. To measure the discrepancy among these configurations, the Procrustes analysis was used, measuring the adjustment among the two configurations by applying the residual sum of squares (M^2), which measures the loss of information on the data structure when only the selected q variables are used instead of p among the two configurations. The diagram below shows the steps of the procedure:

$$\begin{tikzcd}
\mathbf{X}(n\mathrm{x}p) \arrow[r, "\text{select}"] \arrow[d, "\text{PCA}"'] & \tilde{X}\,(n\mathrm{x}q) \arrow[d, "\text{PCA}"] \\
\mathbf{Y}(n\mathrm{x}k) \arrow[r, leftrightarrow, "\text{Procrustes}"'] & \tilde{Z}(n\mathrm{x}k)
\end{tikzcd}$$

Y being the matrix $n \times k$ and $\tilde{Z}$ the dimension matrix $n \times k$, then

$$M^2 = \operatorname{tr}\left\{\mathrm{YY}' + \tilde{Z}\tilde{Z}' - 2\tilde{Z}\mathrm{Q}'\mathrm{Y}'\right\} \tag{7.5}$$

A stopping rule to determine an appropriate value for *i*, given *k*, has been discussed by Krzanowski [7.23], who showed that the number of variables *k* that should be retained in this process is related to the following equation:

$$\left(1+e^2\right)\sigma^2\chi^2_{(a)} \tag{7.6}$$

with $[nk - 0.5k(k+1)]$ degrees of exemption and $e = \sqrt{(p-i-k)/(p-k)}$, where *i* is the number of eliminated variables. According to Krzanowski, if the removed variable is important for explaining the data structure, the sum of residues will be higher than the critical values (C_V). Thus, Krzanowski establishes a stopping rule for Procrustes analysis: the process of variable removal continues until $M^2 > C_V$. In the expression above, the critical value σ^2 is unknown. However, it can be substituted by its estimator [7.23].

With the purpose of verifying the possibility of the reduction of data dimensionality in compositional analysis or, in other words, to eliminate variables without altering the data structure, the data were analysed through a Procrustes analysis, for selection of the variables of interest. Table 7.1 shows the procedure for selection of variables including the elimination sequence, the bidimensionality distance of the configuration of the main components using all the data (M^2) and the critical value (C_V) of 5% (stop rule C_V). In Table 7.1, lanthanum is the first element to be eliminated, since the M^2 value was 30.9, which measures the proximity of the bidimensionality of the configuration of the principal components. This leads to the fact that, for lanthanum, 1087.3 is the C_V with a significance level of 5%. Since M^2 is lower than this value, the elimination of lanthanum does not significantly affect the configuration of the principal components. Once variables have been eliminated by the configuration distance of the principal components, M^2 increases and the critical value decreases, which depends, in turn, on the number of variables, which also decreases.

When the variable is eliminated, the associated configuration is altered to the point that it becomes unacceptable, which occurs when M^2 is larger than C_V. This procedure suggests that La, Sc, Na, Tb, U, Lu and Cs should be eliminated, and that Eu, K, Yb, Cr, Fe and Th should be considered.

TABLE 7.1. SELECTION OF VARIABLES WITH ELIMINATION SEQUENCE

Variable	La	Sc	Na	Tb	U	Lu	Cs	Eu	K, Yb, Cr, Fe, Th
M^2	30.9	82.5	151.3	231	308	409.1	513	667.7	
C_V	1087.3	1023.3	959.4	895.4	831.4	767.5	703.5	639.6	

To verify if the behaviour of the selected variables represents the complete data structure, a new analysis of principal components was made using the data matrix with 316 samples and the six selected elements (Eu, K, Yb, Cr, Fe and Th). Figure 7.3 shows principal component 1 versus principal component 2 of the selected variables. The formation of three compositional groups can be clearly observed, confirming that the result of the PCA using the six elements reproduces results that are similar to those from PCA using all the variables. This shows that the reduction of variables is viable, permitting a savings of human and materials resources, besides allowing for a reduction in the time spent on analysis. This reduction technique of data dimension can be useful with authenticity tests of ceramic artefacts, because a small number of variables can be used for this purpose.

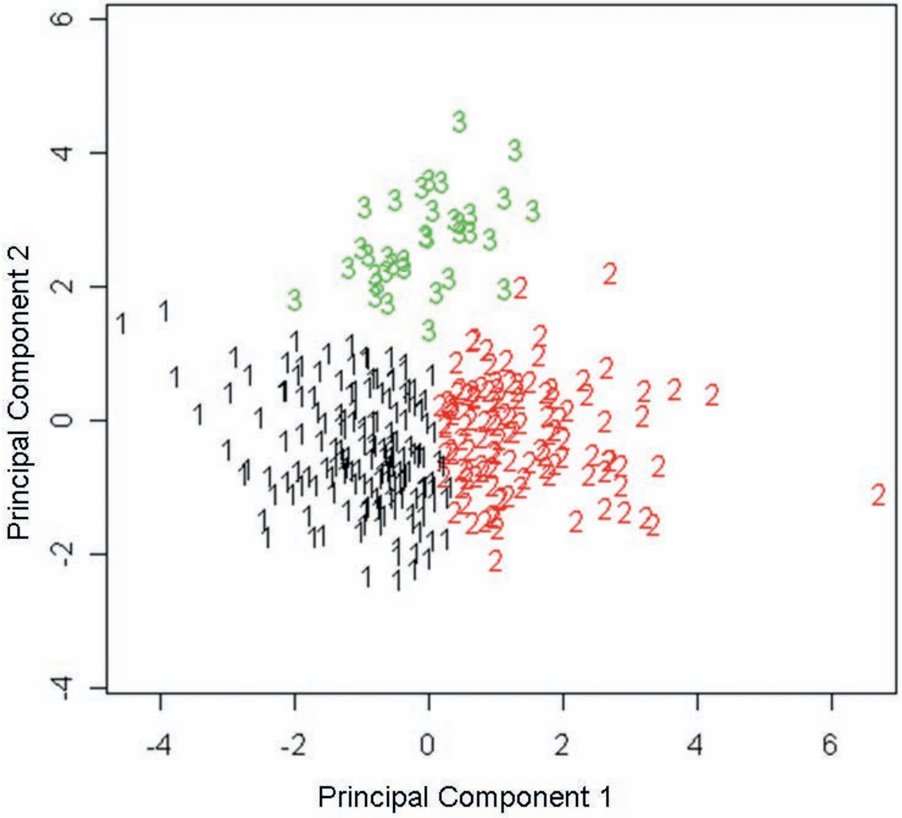

FIG. 7.3. Principal component 1 versus principal component 2 using the selected variables (Eu, K, Yb, Cr, Fe and Th). Groups 1 and 2 are archaeological ceramics and group 3 contemporary Marajoara ceramics.

The results for ESR showed that the firing temperature varied between 450 and 700ºC for the archaeological ceramics as well as for the contemporary ones. However, the firing temperature is not a parameter that can differentiate archaeological Marajoara ceramics from contemporary ones.

7.5. CONCLUSIONS

In this work, it was verified that the precision of the analytical method for the elements studied was good. Both principal components and DA showed the existence of two distinct groups of Marajoara archaeological ceramics, indicating that different sources of raw materials were used in the manufacture of pre-Columbian artefacts. Likewise, the clay used in contemporary Marajoara ceramics is very different from the clay used in the archaeological Marajoara ceramics. The dilution effect produced by the temper in the ceramic concentration data was studied by means of correlation coefficient and showed that the tempering problem does not exist in ceramics. The Procrustes analysis showed that the reduction of variables is viable and the chemical elements Eu, K, Yb, Cr, Fe and Th are sufficient in order to establish a signature for Marajoara pottery. Finally, ESR studies have shown that there is no difference in firing temperature between the Marajoara ceramics (the archaeological and the contemporary ones).

ACKNOWLEDGEMENT TO CHAPTER 7

The authors wish to thank Fundação de Amparo à Pesquisa do Estado de São Paulo — FAPESP, Process 06/57343-3 and 06/58555-4, for financial support.

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Chapter 8

CHARACTERIZATION OF INORGANIC PIGMENTS USED BY SELECTED PAINTERS BY USING ION MICROPROBE AND OTHER COMPLEMENTARY TECHNIQUES

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Abstract

The aim of this chapter is to show results of the collaboration between the Croatian Conservation Institute (CCI) and the Laboratory for Ion Beam Interactions of the Ruđer Bošković Institute (RBI) established within the present CRP. The CCI is the central Croatian institution for conservation and restoration of cultural heritage objects. Prior to restoration/conservation, CCI performs a scientific analysis of an object, primarily to enable selection of the best strategy for its restoration/conservation. On many occasions, such analysis is also helpful to resolve issues such as clarification of authenticity and/or the maker of an object. The CCI has its analytical laboratory, which is fully dedicated to the analysis of cultural heritage and art objects. The CCI analytical laboratory is able to apply various microscopy techniques and photography methods, and is equipped with portable X ray fluorescence spectrometer and X ray radiography instrumentation. Access to complementary microanalytical techniques like Raman spectroscopy or ion beam analytical (IBA) techniques is provided through an already long and successful collaboration with the RBI. The RBI laboratory for ion beam interactions provides complementary analysis of layered microsamples by using IBA techniques, such as particle induced X ray emission and Rutherford backscattering, and for the miniature samples by using ion microprobes.

8.1. INTRODUCTION

The Croatian Conservation Institute (CCI) is the central Croatian institution for conservation and restoration of cultural heritage objects. Prior to restoration/conservation of objects, the CCI performs scientific analyses of them, primarily to enable selection of the best strategy for their restoration/conservation. On many occasions, such an analysis is also helpful to resolve issues such as clarification of authenticity and/or the maker of an object. Scientific analysis of artistic and cultural heritage objects is organized by the CCI through their Natural Science Laboratory. The CCI Natural Science Laboratory is equipped with photography apparatus for the infrared reflectography (IRR) and infrared fluorescence (IRF) techniques, also including optical microscopes for various microscopy techniques based on investigation of objects by using visible, or ultraviolet (UV), light. In addition, the CCI is equipped with an X ray imaging system and with a modern portable X ray fluorescence spectrometer (XRF) used for in situ chemical analysis of surfaces. Access to complementary microanalytical techniques like Raman spectroscopy or ion beam analytical analysis (IBA) is provided through an already long and successful collaboration with the Ruđer Bošković Institute (RBI). The RBI Laboratory for Ion Beam Interactions (LIBI) provides complementary analysis of layered microsamples by use of IBA techniques, such as particle induced X ray emission (PIXE) and Rutherford backscattering (RBS), performed for miniature samples by using ion microprobes.

One of the first successful collaborations between the LIBI staff and the CCI was between 1985 and 1986, when the RBI participated in a project entitled “Secret Paintings of Josip Račić and Miroslav Kraljević — Analysis by Physical and Chemical Methods”. The project goal was to perform scientific analysis of paintings done by two important Croatian painters that were active in the period from the end of the nineteenth to the beginning of the twentieth century, to identify the methods and materials used by artists, to compare them and to present the results to the general public. It included analysis by X rays, infrared and UV light. The RBI analysed the elemental constituents of pigments in 28 paintings. Analysis of pigments was a very important part of the overall analysis. The project ended with an exhibition (that presented all the scientific work), which was held at the Modern Gallery in Zagreb, between 6 March and 6 April 1986.

Since then, there has been a continuous collaboration between the CCI and the RBI in providing supplementary analyses of samples that require elemental characterization. Collaboration is based on characterization of inorganic pigments, alloys and other materials related to paintings, statues, buildings and other objects of cultural heritage. This is done by analysis of microscopic samples at the RBI nuclear microprobe located at one of the beam lines of the RBI tandem accelerator. Recent collaborative work with the CCI includes work on the use of the RBI ion microprobe in a conservation process study of the southern portal of the St. Marco church in Zagreb [8.1], analysis of the Apoximenos statue, which was recently discovered in the Adriatic Sea, and analysis of pigments from numerous paintings, frescoes and polychrome sculptures. In this field, LIBI also collaborates with the Archaeological Museum in Zagreb (in relation to analyses of metallic objects such as helmets, jewellery and various artefacts) and with the Academy of Fine Arts of the University of Zagreb (in relation to analysis of bronze).

In the focus of the present CRP is the collaboration between LIBI, CCI and the Academy of Fine Arts, related to the characterization of inorganic pigments used by selected painters, with the aim to help select the best strategy for restoration/conservation of the related paintings, and at the same time to help clarify suspicious attributions, authorships, possible restoration attempts or interventions in the past. The paintings under analysis were selected between those that were under a regular CCI programme for restoration/conservation, having in mind the particular objectives of the CRP.

During the first half of the CRP lifetime, the work was focused on the analysis of paintings of the seventeenth century early baroque painter Hans Georg Geiger (HGG). He lived in Slovenia but was engaged at the time equally by the Croatian and Slovenian nobilities. He lived in Novo Mesto in Slovenia between 1641 and 1680; most preserved documents bear witness that he had spent a great deal of time in Croatia, working in Zagreb and other towns for Jesuits and Franciscans. In the seventeenth century, both Slovenia and north Croatia belonged to the Austrian monarchy, and artists were allowed to circulate throughout its territory. For various historical reasons, the seventeenth century artistic heritage of Croatia has been reduced to a minimum so that 32 preserved works by this early baroque painter represent an important contribution to the history of art in Slovenia and Croatia. About half of his paintings are in Slovenia and the other half in Croatia. Most of his preserved works have not been signed. Recently, systematic analysis of master HGG paintings has attracted the attention of both Slovenian and Croatian conservators, which resulted in bilateral cultural cooperation. Therefore, the specific work presented here is only a part of the larger collaboration under which several institutions from Croatia and Slovenia conducted scientific and technical research with the purpose of finding out the painter’s use of binding media and pigments, learn about his painting techniques, and hence understand and compare these findings with the existing historical data. The related work has been published [8.2], and here we will present a short summary of the results.

During the second half of the CRP, the focus was moved to the Gothic period paintings from the east Adriatic coast of Croatia. In particular, the work has been focused on investigation of selected paintings originating from the church known as Gospa od Šunja of the island of Lopud near the city of Dubrovnik in Croatia. The related work done under the CRP has been one important part in the direction of restoration of these paintings by the CCI. The paintings in question are presented in Fig. 8.1. Altogether, nine paintings are under investigation and restoration. As Fig. 8.1 shows, they are arranged in a way that one is independent (crucifixion, painting on the right side of Fig. 8.1), and the others consist of four separate painted objects joined together in two wooden painted plates.

According to some documents, these paintings were in the past a part of a more complex altar composition in the Gospa od Šunja church, which had in addition to these paintings an additional smaller polyptych (multipanel painting) with five painted areas. According to historical documents, around 1890 the original altar composition was modified (disassembled) and as a result only this polyptych is now in the church. The complete composition, which includes the polyptych and the above paintings, is shown in Fig. 8.2.

The whole composition is attributed to the painter Matej Junčić, who is supposed to be the founder of the Dubrovnik painting school. This attribution is based on a known manuscript from 1452, where it was written that four Lopud inhabitants ordered and three months later paid Matej Junčić for preparation of an altar with 12 paintings similar to the one which existed at that time in Saint Peter’s Church in Dubrovnik (and which no longer exists). On the other hand, there are strong arguments against such an attribution [8.3]. One is that the whole

Fig. 8.1. Paintings from the island of Lopud investigated during the CCI project.

Fig. 8.2. The paintings under investigation, together with a smaller polyptych in the centre (see text for an explanation).

composition consists of more than 12 paintings, and another points out that the central painting of the small polyptych shows the figure of one donator while the document mentions four donators.

In addition, the paintings have not been in good condition, and they show several layers related to several interventions made in the past. It is known that the first restoration of the paintings was ordered in 1571, and this was one of the first documented restoration attempts in the Dubrovnik Republic. The paintings were partly cleaned and conserved in 1964 and again in 1985. It seems that some restoration work was also done in the nineteenth century (when the original composition was disassembled), which also included the addition of paint overlayers to the original painting. The small crucifixion painting is of much better quality than the other paintings, and there are some suggestions that it does not belong to the composition and that it was perhaps painted by another artist in some other time period. It was decided to perform some scientific investigations of these paintings to help the restoration strategy and to gain some scientific knowledge that could contribute to resolving some doubts about the artist and the authenticity of at least some of the paintings from the composition.

Although our collaboration during the second two years of the CRP was focused on the above mentioned Gothic paintings, we have to mention that in 2007 we collaborated on the topic of investigation of pigments from the wooden inventory of the Trnski Vrh church (originating in the eighteenth century). For this investigation, the use of portable XRF proved to be very useful, since the XRF results acted as a valuable guideline for subsequent targeted sampling actions, thus minimizing the sampling damage. Important questions not answered by XRF (identification of organic pigments, ultramarine, etc.) were subsequently resolved using additional ex situ laboratory methods, primarily micro-PIXE and micro-Raman spectroscopy methods. Details are published in the Ref. [8.4] and will not be further elaborated here.

During the present year (the last year of the CRP), collaboration continued with the joint work on the analysis of eight paintings located in two churches in Dubrovnik. These paintings have been systematically analysed by using a portable XRF system, a proton microprobe, optical and UV microscopy techniques and radiography, with the aim of comparing the use of pigments by an artist or artists of the paintings. Four of the investigated paintings, all located in one of the churches, represent one evangelist. The other four analysed paintings, located in the other church, are very similar to the first four paintings. They represent the same four evangelists as the first four paintings from the other church. Since they also look quite similar to the first set of paintings, there is a common understanding that all these paintings originate from the same period and that they were painted by the same artist(s). In our analysis, we compared pigments of the first set of four paintings with the pigments present on the other set of four paintings. In order to make comparison easier, microsamples for the analysis were taken from similar positions on each of two similar evangelist paintings from the two churches. This work summarized here, and focused on analysis of pigments by X ray spectroscopy methods, is just one aspect of the future larger project that has been planned by the CCI to investigate these paintings from a more global perspective, with the final goal to investigate attributions of these paintings to Mattia Preti. Therefore, it is mentioned only as an illustration of the continuation of our national collaborative activities related to the subject of this CRP.

8.2. ANALYTICAL METHODS USED TO INVESTIGATE PAINTINGS

Altogether 15 master HGG paintings located at various places in Croatia (mostly churches) were analysed by X ray imaging, optical microscopy (OM) methods and PIXE in combination with the nuclear microprobe.

Regarding the paintings from the church on the island of Lopud, the results obtained by X ray imaging and infrared reflectography helped towards the decision to restore the original paint layers by removing overpainted layers and to go ahead with conservation of the original layer with minimal interventions. In addition, it was also decided to prepare a number of microsamples, to investigate the pigments in different layers and to compare the pigments used in different paintings by analysis with OM methods and at the RBI ion microprobe facility, mainly with the goal of obtaining additional scientific knowledge that could contribute to resolving the existing doubts about attribution of at least one of the paintings from the composition (i.e. the small crucifixion painting).

X ray imaging can reveal brushstrokes, overpainting, pentimenti (author's changes to the painting) and in some cases also pigments used. Figure 8.3(a) shows a detail of the painting of St Michael from Gračani (one of the master HGG paintings), while Fig. 8.3(b) shows an X ray image of the same detail. The difference between the church towers indicates overpainting and a possibility that some kind of restoration was done in the past.

Optical microscopy was used to investigate the number and sequence of paint layers in order to ascertain painting techniques, materials and overpainting. The method requires collection of small samples from the painting that should be

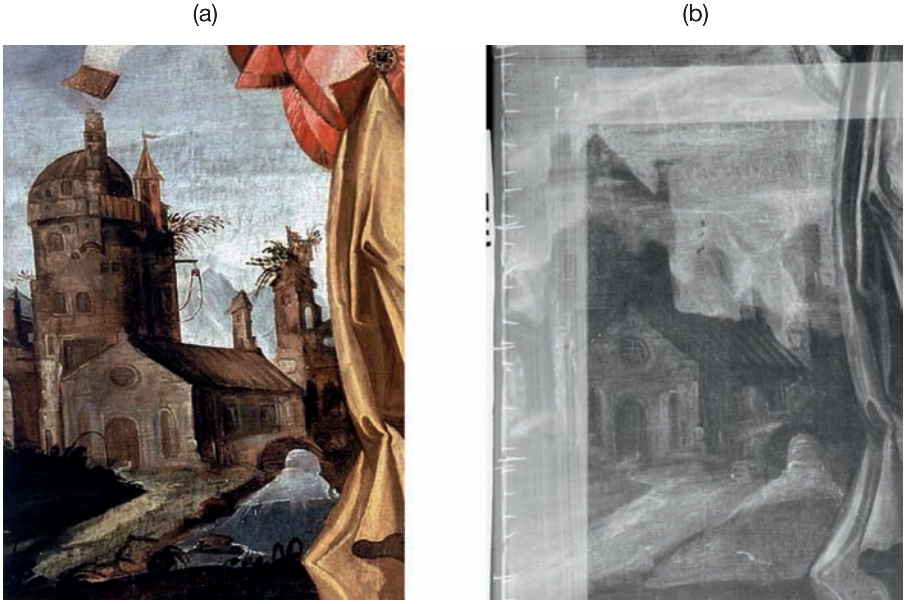

FIG. 8.3. (a) Detail of the painting of St Michael from Gračani; (b) an X ray image of the same detail. The difference between the church towers indicates that some kind of restoration of this painting was done in the past.

embedded in polyester resin and further prepared by grinding and smoothing to a suitable form to investigate the cross-sections of paint layers under the microscope by using visible or UV light. Figure 8.4 shows as an example one such sample taken from one of the paintings from the island of Lopud. Figure 8.4(a) shows the sample as seen under the microscope in visible light, while Fig. 8.4(b) shows the same sample as seen under the microscope in reflected UV light. About 100 such samples have been prepared from the 15 paintings of the master HGG and 21 samples from the paintings of Lopud.

The same conventional samples of paint layer cross-sections embedded in polyester resin as prepared for OM were used for the analysis using the focused proton beam from the ion microprobe. By the detection of characteristic X rays of elements present in the samples by the PIXE technique, two dimensional (2-D) images of elemental distributions at the microscopic level have been obtained and local elemental concentrations determined from the corresponding PIXE spectra (Fig. 8.4). The pigments used by the painters were identified on the basis of OM investigations and of 2-D PIXE images and the corresponding spectra.

When an energetic ion beam (of several MeV energy) hits a target, individual ions penetrate through the target material in their incident direction, gradually losing energy until they stop at a certain depth, which is typically of the order of 0.1 mm (depending basically on the initial energy of the ion and the target material). One of the most probable processes that takes place along the

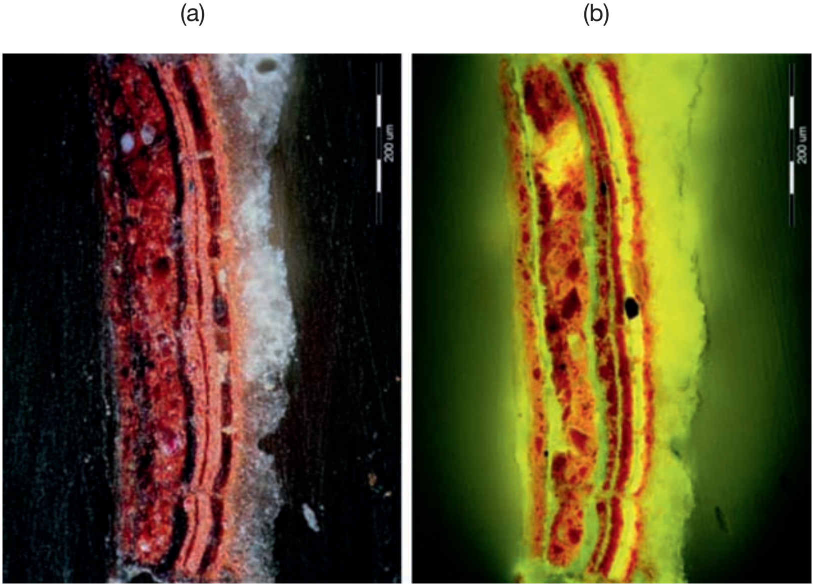

FIG. 8.4. (a) Optical microscopy image of one of the microsamples as seen in visible light. (b) Optical microscopy image of the same sample as seen in reflected UV light.

path of an incoming ion (proton) is its scattering on electrons. As a result of this scattering, atoms are ionized, with electrons being ejected from atoms. The ionized atom tends to return to its original state, by filling the created vacancy with electrons from the outer shells. The excess energy will be given to an emitted photon (X ray emission) or an electron (Auger electron emission). The energy of the emitted X ray depends on the atom type and allows elemental characterization when X rays are detected with an appropriate detector. This is the basis of PIXE spectroscopy [8.5], a multielemental non-destructive detection method capable of measuring concentrations of elements from sodium to uranium with a sensitivity down to the ppm scale.

Samples for analysis have to be inserted into the vacuum chamber, which is seen in the centre of Fig. 8.5(b). Inside the chamber, detectors for X rays and for scattered, recoil and transmitted particles are located. As X ray detector, a 10 mm^2 silicon drift detector (SDD) is used, which can, contrary to conventional Si(Li) detectors, work with high count rates (more than 10 000 counts/s) and does not need liquid nitrogen for cooling. Sample size can range from micrometer dimensions up to 1–2 cm. The data acquisition system SPECTOR developed at the RBI [8.6] enables recording of all signals from detectors, together with the ion beam position at the moment of a particular event. This allows display of 2-D images of information given by a particular detector. For the measurements, a 3 MeV proton beam of about 50–100 pA current was focused to a spot size of a few μm^2 by quadrupole lenses. The beam was scanned over a sample by the computer controlled scan generator (Fig. 8.5(a)). The collection time for each measurement was between 10 and 30 min. All the spectra were recorded in the list mode, to enable later off-line computer analysis.

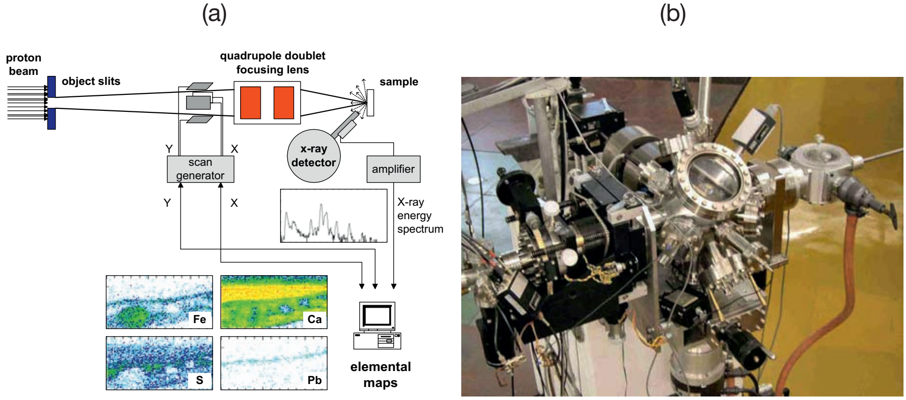

FIG. 8.5. (a) Principles of the ion microprobe generation of 2-D elemental maps. (b) RBI ion microprobe end-station.

After the measurements, a computer analysis of measured data was performed:

(a) To extract 2-D images of elemental distributions at the microscopic level;
(b) To estimate local elemental concentrations (determined from the corresponding PIXE spectra by using the GUPIX analysis code [8.7]) at selected points of interest within 2-D images of elemental distributions.

The off-line computer analysis was done by using the above mentioned SPECTOR data acquisition and analysis software. During the measurement, all the spectra were recorded in list mode. SPECTOR may use such list mode obtained data files to simulate (or as we say replay) measurements on a computer. In such a way, it is possible to redefine regions of interest in spectra and to choose different areas of interest of the scanned target areas to obtain specific information about the elemental composition in selected target areas without performing additional measurements.

As an illustration of the technique, Fig. 8.6 shows elemental maps of Hg, S (+Pb+Hg), Fe, Si, Pb, Cu, Ca and Al corresponding to the measurements of one of the microsamples taken from one of the three restored paintings, parts of a composition originating from the Gospa od Šunja church on the island of Lopud near Dubrovnik.

In addition to microsamples, small amounts of ‘dust’ samples were taken from the selected areas of the Madonna (drapery) from the crucifixion painting and from the St. Catherine (drapery) from the panel painting (left hand paintings in Figs 8.1 and 8.2). Both samples were taken from areas with dominating blue pigments and they were analysed by use of PIXE at the ion microprobe to compare elemental compositions. Figures 8.7 and 8.8, respectively, show the corresponding elemental maps and X ray spectra. Figure 8.9 shows elemental maps of the zoomed area from the ‘dust’ sample related to the Madonna drapery, with the corresponding PIXE spectrum compared with the spectrum from Fig. 8.8.

8.3. RESULTS AND DISCUSSION

As already explained in Section 8.1, the results of the analysis related to the master HGG paintings are reported in Ref. [8.2]. A number of pigments used in the paintings have been identified. We can summarize the findings as follows:

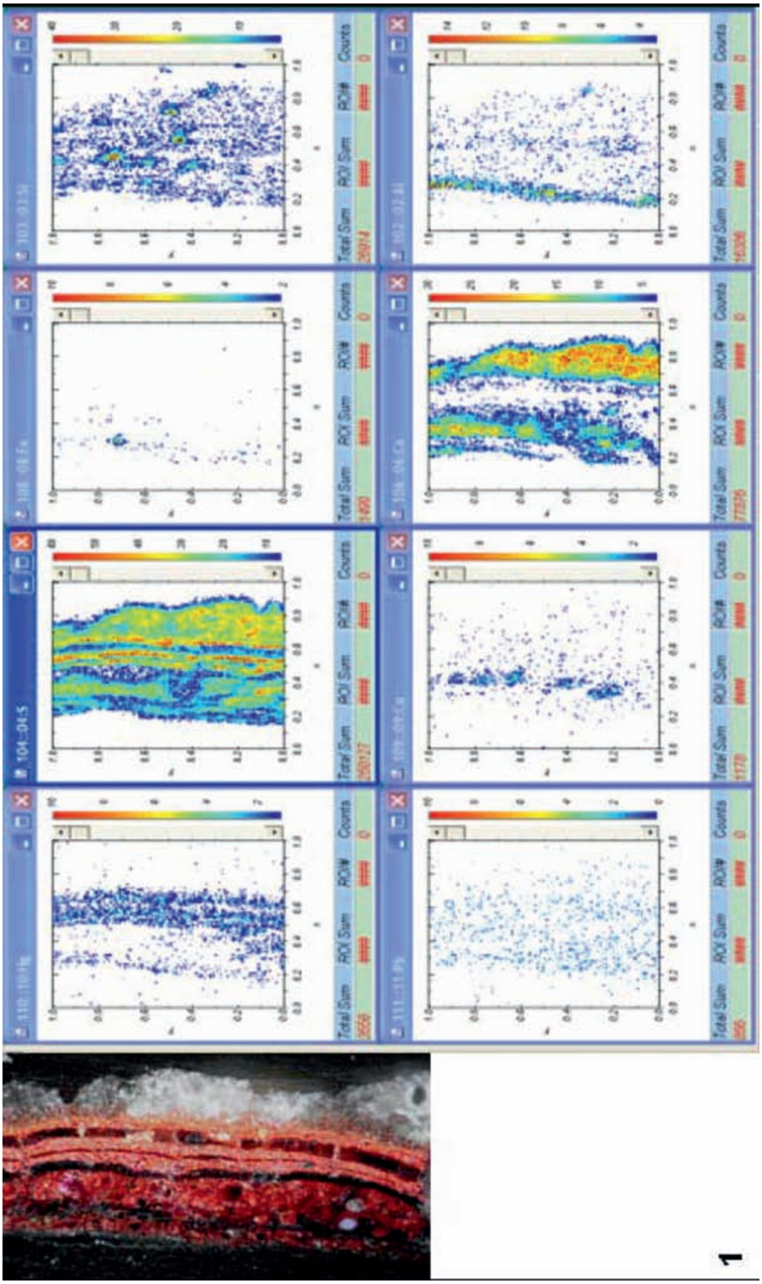

FIG. 8.6. Elemental maps of Hg, S (+Pb+Hg), Fe, Si, Pb, Cu, Ca and Al in one of the microsamples taken during restoration from one of the paintings of the polyptych originating from the Gospa od Šunja church on the island of Lopud near Dubrovnik.

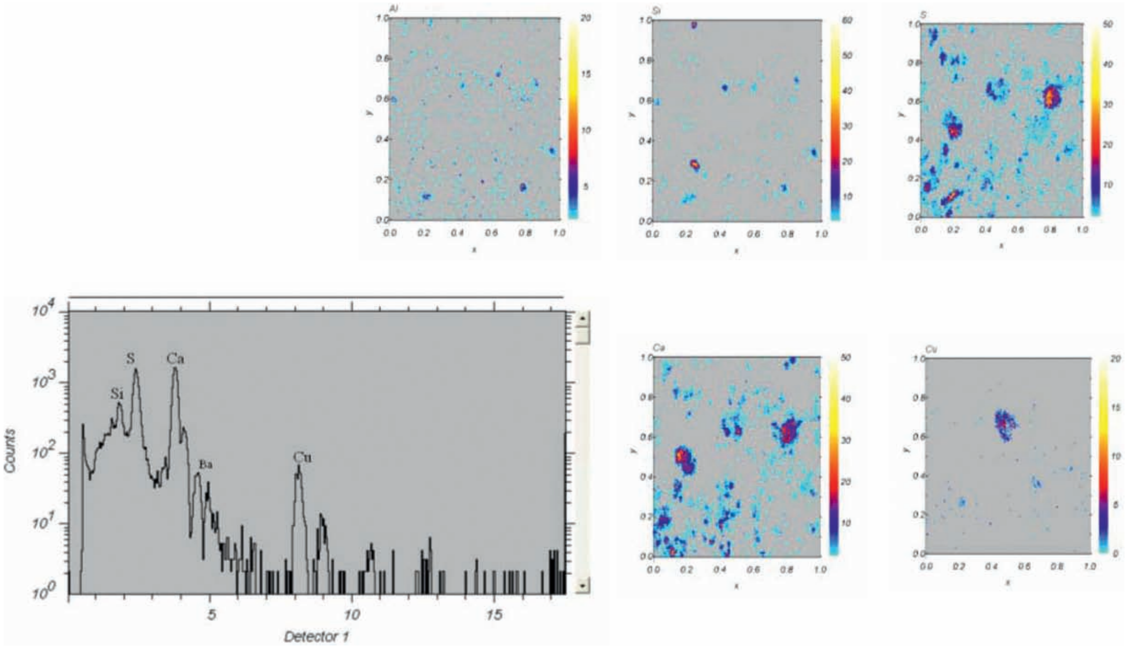

FIG. 8.7. Elemental maps and the corresponding PIXE spectrum of the ‘dust’ sample corresponding to the blue pigment area of the Madonna drapery from the crucifixion painting.

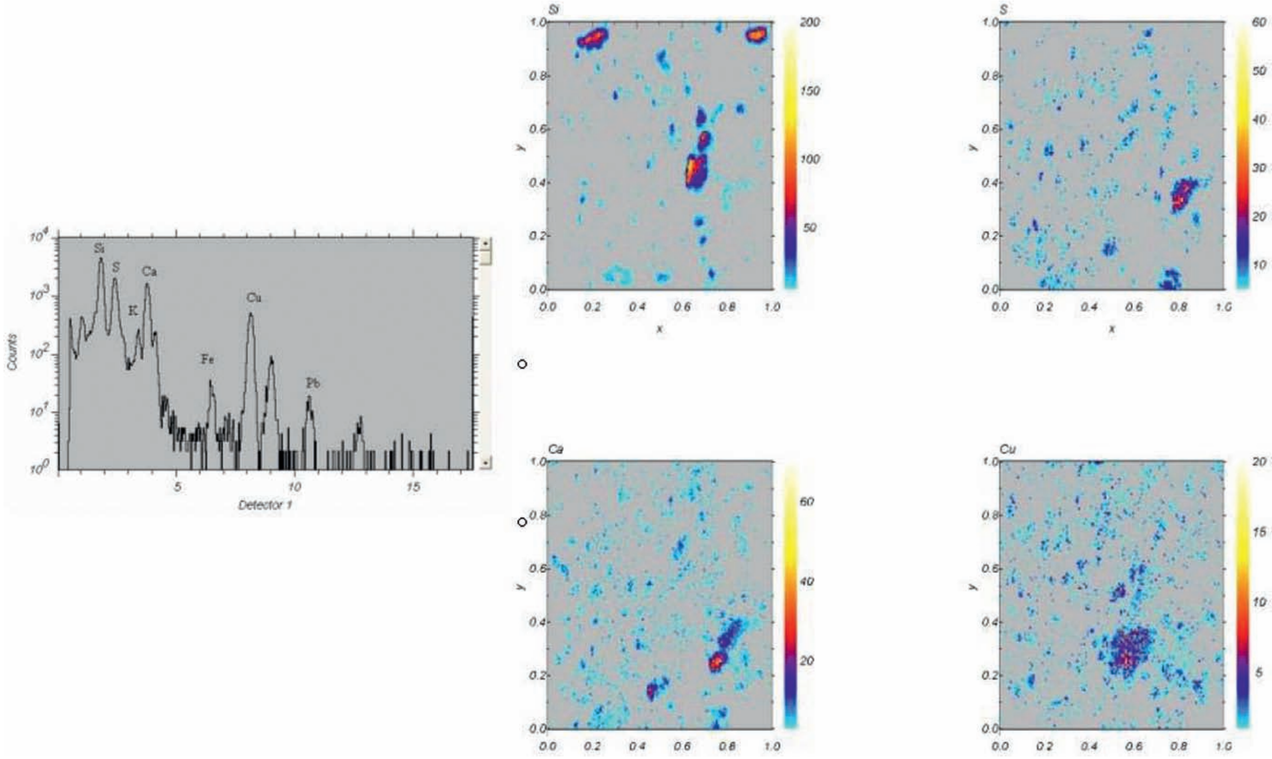

FIG. 8.8. Elemental maps and the corresponding PIXE spectrum of the ‘dust’ sample corresponding to the blue pigment area of the St. Catherine drapery from the painting in the left hand panel of Fig. 8.1.

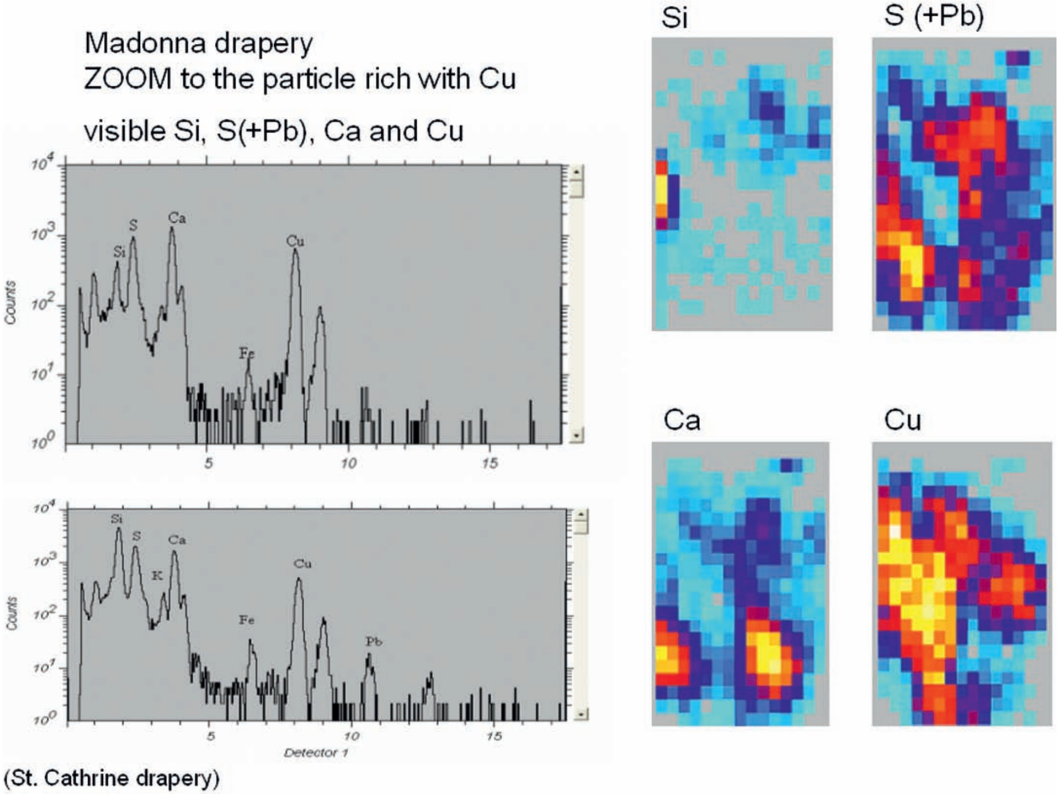

FIG. 8.9. Elemental maps of the zoomed area from the ‘dust’ sample related to the Madonna drapery, with the corresponding PIXE spectrum compared with the spectrum from Fig. 8.8.

(a) It has been determined that lead white is the only white pigment in almost all of the paintings. This is in agreement with the findings of our Slovenian colleagues who investigated the master HGG Slovene opus.
(b) Iron yellow ochre is the yellow pigment identified in five paintings.
(c) Four different red pigments were found: iron red ochre, HgS (cinnabar, vermilion), minium and alizarin. The most common of these is iron red ochre, which was found in six paintings. In one of the paintings, the artist used three different red pigments.
(d) The most commonly used blue pigment identified is smalt. The other two blue pigments identified are ultramarine and azurite.
(e) The identified palette contains two green pigments: green earth and copper resinate.

Regarding the analysis of the paintings from the Gospa od Šunja church, the results can be summarized as follows: a number of pigments have been identified and information about restoration activities in the past have been obtained. The following pigments were found in analysed samples:

White:

— Lead white ($2PbCO_3 \cdot Pb(OH)_2$);
— Gypsum ($CaSO_4 \cdot 2H_2O$);
— Barium white ($BaSO_4$) (nineteenth century).

Red:

— Cinnabar (HgS);
— Red ochre ($Fe_2O_3 \times nH_2O$);
— Bolus ($Al_2O_3 \times SiO_2 + Fe_2O_3$);
— Organic red;
— Alizarin ($Al(OH)_2$);
— Minium (Pb_3O_4).

Blue:

— Azurite ($2CuCO_3 \times Cu(OH)_2$) – ($CaCuSi_4O_{10}$) (cuprorivaite?);
— Ultramarine ($2Na_2Al_2Si_2O_6 \times NaS_2$).

Brown and yellow:

— Iron oxide (brown and yellow ochre).

Black:

- Organic black.

Metals:

- Gold (Au);
- Copper and zinc (Cu + Zn), in compounds, characteristic of the nineteenth century.

Two dimensional maps of elemental composition confirmed that paintings were overpainted with several layers, and that the last layer was done in the nineteenth century, as can be concluded from the fact that some pigments and materials discovered at the end of the eighteenth/beginning of the nineteenth century were used.

A high concentration of calcium and sulphur proved the usage of a gypsum-like filling in the base, where the presence of sulphur and silicon indicated addition of some silicates, while the high content of lead shows extensive use of lead white in combination with other pigments such as azurite.

Regarding the analysis of ‘dust’ samples collected from the Madonna (drapery) from the crucifixion painting and from the St. Catherine (drapery) from the left panel painting: as explained, both samples were taken from areas with dominating blue pigments and analysed by PIXE at the ion microprobe to compare elemental compositions. Conclusions from the analysis of these samples could be summarized as:

(a) The spectra and 2-D maps corresponding to two samples from the Madonna and from the St. Catherine are very similar.
(b) In both cases copper is the signature element for the blue pigment, which is most probably azurite, and which is occasionally mixed with lead-containing pigment (lead white).
(c) From the analysis of spectra and 2-D maps, it can also be seen that samples contain some particles from the base of the paintings under the blue pigment, which is basically gypsum (Ca + S), and traces of gold (Au) from the surface.
(d) The spectrum of the Madonna drapery shows some presence of barium, which is not seen on ‘dust’ samples from the St. Catherine drapery. However, the presence of barium was seen on the surface of some corresponding microsamples.

(e) The results would not be in favour of the assumption that the ‘crucifixion’ does not belong to the composition and that it was perhaps painted by some other artist in some other time period.

8.4. CONCLUSIONS

The nuclear microprobe in combination with PIXE and RBS analysis is a valuable tool that can help in identification of pigments in paintings. Since the technique preserves the integrity of the sample, the same samples may be reused for complementary analysis by some other techniques.

In this particular case, the technique has been successfully used in combination with portable XRF spectroscopy, Raman spectroscopy, infrared reflectography, optical microscopy methods and X ray imaging, to identify a palette of pigments in 15 paintings of the Master HGG and wooden inventory in the Trnski Vrh church, all located in north-west Croatia, and those in paintings from the Gospa od Šunja church from the island of Lopud near Dubrovnik, Croatia. By a combination of these, often complementary, methods a thorough characterization of each pigment can be obtained, allowing for a proper strategy of the restoration/conservation treatment. Additionally, the results of such scientific analysis are very helpful to clarify issues related to attributions of paintings and to interventions on the paintings in the past.

ACKNOWLEDGEMENT TO CHAPTER 8

The authors appreciate the role of the IAEA in contributing to this work by supporting a collaboration through the CRP entitled “Applications of Nuclear Analytical Techniques to Investigate the Authenticity of Art Objects” (2004–2008) and through the Regional TC project entitled “Nuclear Techniques for the Protection of Cultural Heritage Artefacts in the Mediterranean Region” (2005–2008).

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Chapter 9

ARCHAEOMETRY APPLICATIONS OF COLD NEUTRON BASED PROMPT GAMMA NEUTRON ACTIVATION ANALYSIS

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Abstract

Prompt gamma activation analysis (PGAA) is based on the detection of prompt gamma radiation following the capture of neutrons into the atomic nucleus. Since every atomic nucleus emits characteristic prompt gamma radiation, this method is suitable for multielemental (panorama) analysis. The PGAA method can be regarded as absolutely non-destructive, because of the relatively low intensity of the beam. The main focus of this project was on the research of ancient ceramics. Pottery production was one of the most important crafts of prehistoric communities. As the first aim of this project, pottery findings from Neolithic and later prehistoric sites in Hungary were investigated with PGAA. Compositions of local sediments, as potential raw material sources, were compared with those of pottery. As the second aim of the project, pottery fragments from the multiperiod site at Vörs, in south-west Hungary, were analysed, together with clay from the surrounding areas. In a firing experiment, an attempt to reproduce the ancient production techniques was made. As a third aim of the project, PGAA was tested from a methodological point of view. The reliability of the method has been occasionally checked through parallel measurements of archaeological samples with instrumental neutron activation analysis and X ray fluorescence analysis as well. The authors took part in a proficiency test, organized by the IAEA, on a porcelain material.

9.1. INTRODUCTION

One of the key problems of archaeological artefact analysis by instrumental techniques is the identification of raw materials. Indeed, the provenance of the artefacts is an excellent indicator of the movements and contacts of prehistoric peoples. In recent years, the importance of applied modern analytical techniques has been growing continuously relative to traditional typology studies. Scientists seek information regarding the material of the object, for example chemical (elemental and isotopic) composition, petrography and phase structure, preferably without destruction of any part of these valuable objects.

Prompt gamma activation analysis, a nuclear method applicable for ‘bulk’ analysis of a few cubic centimetres of material, is an ideal, absolutely non-destructive tool to determine the average composition of different kinds of materials. In this CRP, it was decided to investigate archaeological ceramics and their raw materials, mainly with PGAA. The applicability of PGAA in the archaeometry of pottery has already been proved [9.1, 9.2]. As comparative methods and reliability checks, the more widespread instrumental neutron activation analysis (INAA) and X ray fluorescence (XRF) analysis were applied to a number of samples.

Starting from the Early Neolithic period, pottery production has been one of the most important crafts of prehistoric communities. Pottery remains represent the most abundant part of the unearthed treasure from the Early Neolithic period. In archaeometry studies, the key questions to be answered are the identification of raw material sources, workshops, technologies, and the separation of local products from imported ones.

This project deals mainly with regional factors, comparing local sediments with the material of early ceramics from all over Hungary. Hungary is known to have served as a secondary centre for Neolithization in Europe, forwarding ideas and knowledge about ceramics production from the south-east to the north-west. The main focus of analysis has been on material from recent excavations, with adequate documentation and abundant comparative samples. In our research plan, we outlined the following tasks:

(a) Investigation of pottery findings from excavations of eight major Neolithic sites in Hungary (Fig. 9.1, Map 1). The material to be studied was planned to include recent acquisitions from Vörs, Kup, the Aggtelek-Baradla cave and Tiszalúc, all from the Neolithic period, and comparative material from various classical sites of early Neolithic cultures. We could also rely on samples from Szarvas-Endrőd, Tiszaszőlős-Domaháza, Felsővadász and Tihany-Apáti. Additionally, sampling of local sediments, as potential raw material sources was planned.

(b) One of the above mentioned sites, Vörs, is situated on the south-west shore of Lake Balaton (Fig. 9.1, Map 2). It is representative not only of the Neolithic Age, but also of pottery findings from various periods from Early Neolithic (6000 B.C.) up to the Hungarian Conquest Period (A.D. 1000). The unique feature of this multiperiodic site is that it provides the opportunity to perform a comparative study of various cultures. It was planned to sample the seven main periods at this site, with many samples representative of each period.

(c) The third part of the research deals mainly with methodology. To check the performance of PGAA on ancient pottery, and comparison with INAA as well as with XRF, we planned to measure 'Terra Sigillata' pottery and other selected samples. The INAA experiments were done by M. Balla, of the Institute of Nuclear Techniques, Budapest University of Technology and Economics. The XRF measurements were done by H. Taubald at the University of Tübingen. A detailed study of complementary features of the three methods was performed.

(d) Additionally, we took part in proficiency test measurements in-between the other participating laboratories. This proficiency test experiment was organized by the IAEA on a standard porcelain reference sample, distributed among the participants.

In general, we have to say that, during the project period, fewer PGAA measurements have been accomplished than were originally planned, because of the unexpectedly long duration of the upgrade of the neutron guide, which was done in three steps.

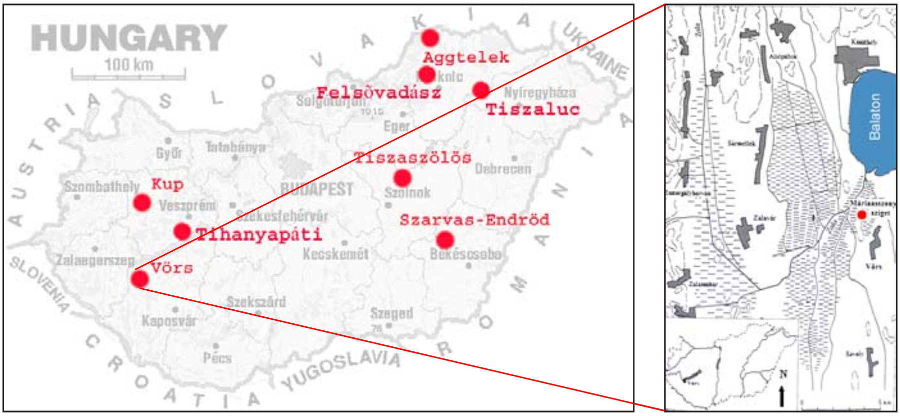

Fig. 9.1. Maps 1 and 2 (on left and right, respectively) of the Neolithic localities in Hungary it was planned to investigate.

9.2. EXPERIMENTAL METHODS USED

The major analytical tool applied for this project was PGAA, other complementary methods are described briefly.

The PGAA measurements were performed at the 10 MW Budapest Research Reactor. In most cases, the samples were irradiated in a cold neutron beam, which was guided 30 m away from the reactor core to the experimental station. The neutrons, which exit the reactor core, are moderated by a liquid hydrogen cell and are cooled down to 20 K. Because of the $1/v$ dependence of the neutron absorption cross-section, the sensitivity of the method has increased by a factor of 20, compared with the sensitivity of the thermal beam. Until the end of 2006, the thermal equivalent flux of the cold beam was 5×10^7 cm^{-2}·s^{-1}. Following the first two upgrades of the neutron guides, between January and October 2007, we used a thermal equivalent flux of 7×10^7 cm^{-2}·s^{-1}, while following the third upgrade, we reached the 1.2×10^8 cm^{-2}·s^{-1} intensity. A detailed description of the analytical system was given by Révay et al. in 2004 [9.3].

Most of the objects were irradiated in atmospheric conditions with a 2 cm × 2 cm beam. Since the sample is transparent to neutrons, an average bulk composition of the investigated volume is obtained. The emitted gamma radiation is detected with a complex high purity germanium–bismuth germanate detector system; the signals are processed with a multichannel analyser. The spectra are evaluated with Hypermet-PC software; the element identification is based on our prompt gamma library [9.4]. The detected gamma ray intensity A_E is directly proportional to the mass of a given element m, the analytical sensitivity S and the measurement time t:

$$A_E = mSt \tag{9.1}$$

and

$$S = \frac{N_\mathrm{A}}{M}\theta\sigma_0 I_\gamma \Phi_0 \varepsilon(E_\gamma) \tag{9.2}$$

The analytical sensitivity S is expressed in units of counts·s^{-1}·g^{-1} in Eq. (9.2). It is proportional to the neutron capture cross-section of the nucleus σ_0, the isotopic abundance θ and the gamma yield I_γ, which are nuclear constants, as well as to the neutron flux Φ_0 and the detector efficiency $\varepsilon(E_\gamma)$, which are characteristics of the measuring system. Further symbols in Eq. (9.2) are: the Avogadro number N_A and the atomic mass of the given element M. The mass ratios, or equivalently the weight percentage ratios of arbitrary elements '*X*' and '*Y*', will be independent of the actual amount of the sample and also of the exact neutron flux. It can be calculated from peak area ratios and sensitivity ratios:

$$\frac{w_X(\%)}{w_Y(\%)} = \frac{m_X}{m_Y} = \frac{A_X}{A_Y}\frac{S_{\gamma,Y}}{S_{\gamma,X}} \tag{9.3}$$

The sensitivities for the most intensive prompt gamma lines of all chemical elements were determined by internal standardization measurements at the Budapest Research Reactor and are collected in a new gamma ray spectrum catalogue for PGAA [9.4]. When all the major elementary components are determined by PGAA, it is not necessary to measure a standard comparator material with the sample, since the concentrations can be determined using Eqs (9.3) and (9.4):

$$\sum_i w_i(\%) = 100 \tag{9.4}$$

This criterion is usually fulfilled in the case of geological samples and also in the case of ceramics, except the poorly detectable oxygen. The concentration of oxygen is calculated according to the usual oxidation states of major components. The sensitivities, and the equivalent detection limits of PGAA, vary over a wide range for different elements.

As a basic feature of PGAA, it was not necessary to take subsamples from pieces of ceramics, they were simply mounted inside the sample holder, in a fixed position. The acquisition time was chosen so as to achieve satisfactory counting statistics. The typical acquisition time was between one and three hours. Soil (or clay) samples had been dried at 105ºC overnight, then powdered, homogenized and packed into FEP film.

In the case of two large archeological objects — Roman 'Terra Sigillata' plates — the sample holder was removed and the objects were placed in the way of the neutron beam; by geometrical means it was possible to identify the analysed part of the objects. In the case of every experimental set-up, the detector efficiencies and background conditions were determined and were taken into account.

The INAA measurements were made by M. Balla, of the Institute of Nuclear Techniques, University of Technology and Economics, Budapest. The training reactor is a pool type reactor with a maximal thermal power of 100 kW and a thermal neutron flux of 2.4×10^{12} $\text{cm}^{-2}\cdot\text{s}^{-1}$. The irradiation time for ceramics samples was eight hours, and gamma spectroscopic measurements were made after 7 and 30 days. A Canberra HPGe well type detector (with a resolution of 1.95 keV and a relative efficiency of 20.5%) was applied for gamma spectroscopy, and was connected to a Canberra S100 multichannel analyser. For the evaluation of spectra, Sampo 90 software was used. Standardization was achieved by the single comparator method, using gold as the comparator. The thermal/epithermal flux ratio was monitored by zirconium foils. The precision of the measurements was monitored by irradiating samples of the NBS SRM 1633a coal fly ash standard reference material.

The XRF analyses were made by H. Taubald, of the Institute of Mineralogy, University of Tübingen, Germany (a wavelength dispersive X ray fluorescence analyser, Bruker AXS S4 Pioneer X ray spectrometer, Rh tube at 4 kW on homogenized samples). During sample preparation, 1.5 g of the unheated and powdered sample and 7.5 g Spectromelt melting material (Merck A12, di-lithium-tetraborate: lithium-metaborate ratio of 66:34) were mixed and melted at 1200°C using an Oxiflux system from the CBR analytical service to make homogeneous fused beads. Prior to preparation, the samples were ground with an agate mill for 10 min. Loss on ignition (LOI) was determined at 1050°C externally and is displayed as LOI. The analytical error and detection limits vary and depend on element and sample composition.

9.3. THE INVESTIGATED SAMPLES

In the first task, it was planned to analyse ceramic archaeological finds and local sediments from eight Neolithic sites in Hungary (Vörs, Kup, the Aggtelek-Baradla cave, Tiszalúc, Szarvas-Endrőd, Tiszaszőlős-Domaháza, Felsővadász and Tihany-Apáti) with PGAA and with other complementary methods. Among them, Vörs — located on the south-west shore of Lake Balaton (Fig. 1, map 2) — has a key importance from the archaeological point of view. It is representative not only of the Neolithic Age but also of abundant pottery finds from various periods from Early Neolithic (6000 B.C.) up to the Hungarian Conquest Period (A.D. 1000). The unique feature of this multiperiodic site is that it serves as an opportunity to perform a comparative study of various cultures.

Unfortunately, because of the unexpected shortening of available beam time, we were able to investigate archaeological pottery and raw materials only from Szarvas-Endrőd, Tiszalúc and Vörs. Concerning these circumstances, the sampling was limited to certain archaeological periods: Late Neolithic ceramics from Szarvas-Endrőd, Middle Copper Age to Early Iron Age ceramics from Tiszalúc and Early Bronze Age ceramics from Vörs. The pottery fragments belong to the collections of various museums, first of all to the Hungarian

National Museum. The soil samples have been collected during various field trips in 2005 and 2006. Altogether, 58 archaeological pottery and 12 soil (clay) samples were analysed with PGAA. In order to obtain archaeological consequences, as detailed as possible, we used the INAA, XRF and petrography data for critical evaluation. These investigations were partly done within a Hungarian–German (DAAD–MÖB) cooperation (Table 9.1).

As a specific task in the project, we have planned a series of firing experiments of local clay from Szarvas-Endrőd. In the first step, two pairs of samples (raw and fired at 800ºC) were analysed by PGAA, and the change in composition was checked. In a second step, 13 pieces of modern ceramics were prepared from local clay with different techniques, and then were fired at 800ºC for two hours. Later the chemical composition will be determined with PGAA, while the phase properties will be determined by petrographic studies (thin section microscopy).

TABLE 9.1. NUMBER OF THE INVESTIGATED ARCHAEOLOGICAL AND GEOLOGICAL SAMPLES
(measurements jointly within a MÖB–DAAD project with Tübingen University)*

Locality	Sample type	PGAA	XRF*	INAA*	Petrography*
Szarvas-Endrőd	Pottery	15	33	30	+[a]
Szarvas-Endrőd	Sediment	2	12	In progress	+
Szarvas-Endrőd	Fired sediment	6	8		+
Tiszalúc	Pottery	11	14	6	+
Tiszalúc	Sediment	10	6	6	–[b]
Vörs	Pottery (Kisapostag)	26	15	15 In progress	+
Vörs	Pottery (other studies)	–	54	24	+
Vörs	Sediment	–	10	10 In progress	+
Battyánpuszta	Sediment	–	4	4 in progress	+
Total		70	156	95	

[a] +: Petrography performed.
[b] –: No measurement.

Within the framework of this CRP, the PGAA laboratory at the Institute of Isotopes took part in a proficiency test organized by the IAEA. A standard reference material (SRM) sample, made of Chinese porcelain, was prepared and distributed among the participant laboratories, in order to collect analytical results obtained by different nuclear methods. The performance of the analytical procedures was evaluated by experts from the IAEA, and the outcome was discussed.

As topics loosely related to this CRP, a few other objects, like two Roman Terra Sigillata plates, were analysed by PGAA, as well as Inca pottery fragments.

9.4. RESULTS AND DISCUSSION

With PGAA it was possible to determine the concentrations of all the major components (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and H) and some trace elements (B, Cl, Sc, V, Nd, Sm and Gd — depending on their concentrations) in all ceramics and clay samples. When PGAA data were not available — for instance, soil measurements from Vörs or more trace elements, such as Zr, La, Ce and Yb — we used the results from XRF or INAA measurements. As a result of analytical data comparison from PGAA versus XRF or PGAA versus INAA, PGAA gives reliable concentration values for the most detected components; however, minor systematic deviations can be observed.

Pottery is a composite material since it is, in almost all the cases, a mixture of two or more components (clay and non-plastic grains). When investigating archaeological ceramics, the effects of the mixed raw materials, the modifying manufacture and the processes of the utilization and burial can interfere with the determination of today’s bulk composition. Thus, in order to obtain information about the ‘past life’ of the object, we have to separate the elements connected to the different stages of the history of the pottery.

Basically, elements related to the origin (provenance) of the raw material are the so-called immobile, incompatible elements which are resistant to effects occurring after the manufacture of the pottery. These elements are Si, Ti and Al from the major elements (given in the oxide formula in geochemistry) and V, Sc, Co, Cr, Ni, Zn, Zr, Y, Hf and rare earth element (REE) trace elements. These chemical components remain stable after the formation of the raw materials (clay, silt, sand and rock) and refer to the origin of the applied natural materials.

The other important group of chemical components is not resistant to post-manufacturing effects (e.g. washing of the raw clay, drying, firing, applications for cooking or liquid storage, or burial in soil-forming conditions) because they are partly mobile and partly compatible elements. These are Fe, Ca (partly K and Na) and P from the major elements (given in the oxide formula in geochemistry) and B, Cl, Ba, Sr and Rb from trace elements. Magnesium is also a rather mobile component, which can be mobilized during high temperature firing. The changes in manganese concentration are strongly reflected in the actual redox potential conditions. Performing a geochemical evaluation, it is important to keep in mind that these components can be easily dissolved or precipitated during the 'life' of the ceramic, and in this way they can provide information on the utilization or burial circumstances of the object.

In order to obtain archaeometrical consequences from the results, the three independent prehistoric sites (Szarvas-Endrőd, Tiszalúc and Vörs) were investigated separately. Concerning the above detailed aspects of chemical elements, the provenance investigations of archaeological ceramics required the application of concentrations and ratios of immobile and incompatible elements during the geochemical interpretation. For this reason, various bivariate plots were constructed.

In the case of Vörs, the archaeological ceramics were selected from two separate parts of the site (Vörs-Máriaasszonysziget and Vörs-Tótok Dombja). One of the basic questions was if it is possible to make a distinction between the pottery of the two 'subsites'. The other question was about the potential raw materials applied for pottery making. The two candidates for the original raw material were the local clayish–sandy soils from Vörs and the clayish sediment from the closest known clay mine at Battyánpuszta.

To answer these questions, a TiO_2/Al_2O_3 versus Zr/V bivariate correlation diagram (Fig. 9.2) was constructed. It was not possible to separate the pottery of Vörs-Máriaasszonysziget and Vörs-Tótok Dombja on a geochemical basis. However, there was a group of two sherds from Vörs-Máriaasszonysziget, which diverged from the main cluster of ceramics by almost all of the incompatible elements and their ratios. This group comprises those sherds which proved to be 'carbonatic sand tempered' by microscopic petrographic investigations [9.5]. This feature separates them from the major part of the ceramics from Vörs, which are 'crushed pottery tempered'. The second part of the geochemical interpretation dealt with the identification of the potential raw material. It became clear that local soils near the archaeological site are not the proper raw material from a geochemical point of view. However, the clays from Battyánpuszta are quite similar to those of the pottery — especially to the carbonate sand tempered ceramics. This makes it probable that the not too far distant clay source at Battyánpuszta could have provided raw material for the ceramic manufacture in Vörs during the Early Bronze Age.

In the case of Szarvas-Endrőd, the investigated archaeological ceramics were selected from the different parts of the complex Late Neolithic site extending to a large territory. The main questions were aimed at examining again

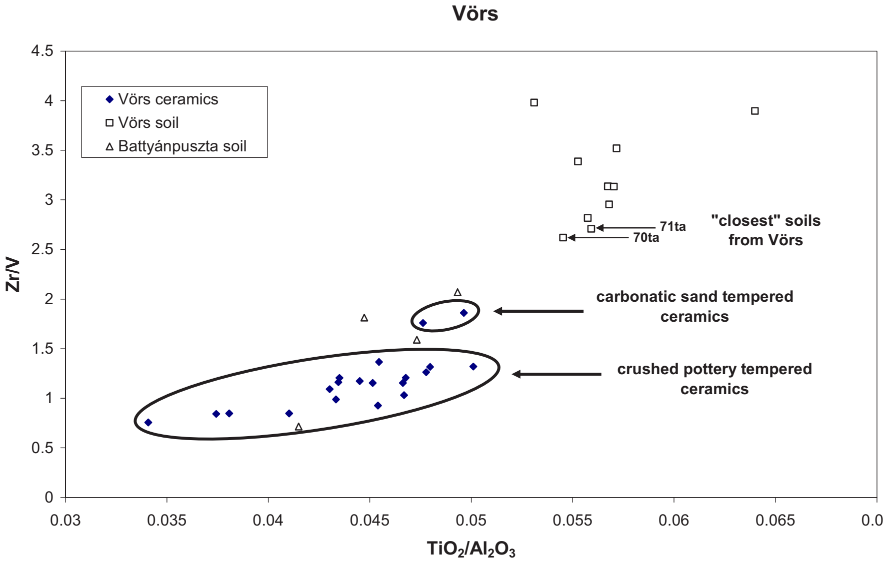

FIG. 9.2. TiO_2/Al_2O_3 versus Zr/V ratios for sediments and ceramics from the Vörs region (in Hungary).

the ‘in-site’ differences among the ceramics and the possibility of application of local clayish–silty (loess) soils as raw materials.

To answer these questions, the TiO_2 versus Al_2O_3 bivariate correlation diagram (Fig. 9.3) is presented here. Although former microscopic petrographic investigations did not outline mineralogical compositional differences among the ceramics and classified them only by their grain size, their chemical composition ranged over a wide area of the ‘compositional space’. However, it was not possible to separate exact groups of the samples. According to the investigations into potential raw material sources, the most probable sources were verified to be the Pleistocene infusion loess and Holocene clays from exact sites. This separation suggests an intentional selection of the local raw material by the potters at the Late Neolithic site of Szarvas-Endrőd [9.6].

In the case of Tiszalúc, the examined sherds derived from Middle Copper Age and some later (Late Copper, Early Bronze and Early Iron Age) ceramics. One of the basic questions was if it is possible to make a distinction among the pottery of the different archaeological periods. The other question was about the application of the local raw materials for pottery making in the subsequent cultures.

To answer these questions, a SiO_2/Al_2O_3 versus K_2O/Na_2O bivariate correlation diagram (Fig. 9.4) is presented. Observing the geochemical

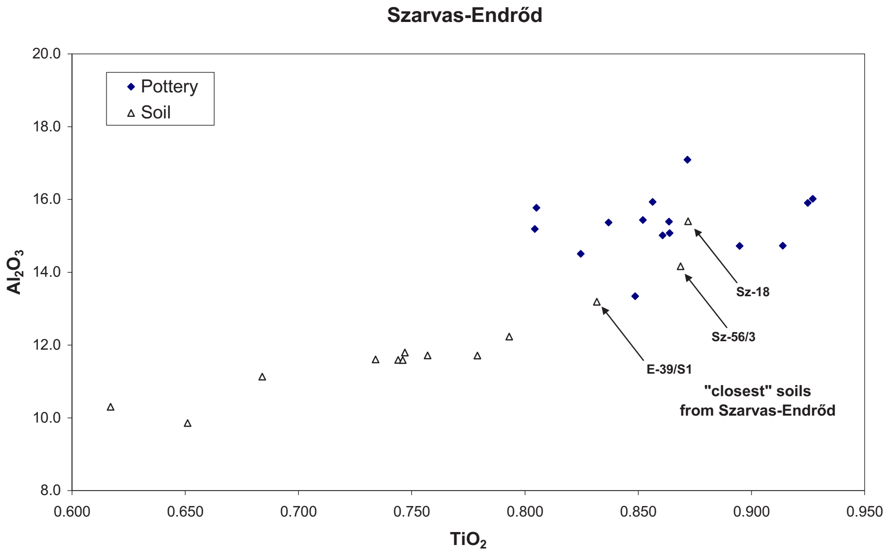

FIG. 9.3. *TiO_2 versus Al_2O_3 concentrations for sediments and ceramics from the Szarvas-Endrőd region (in Hungary).*

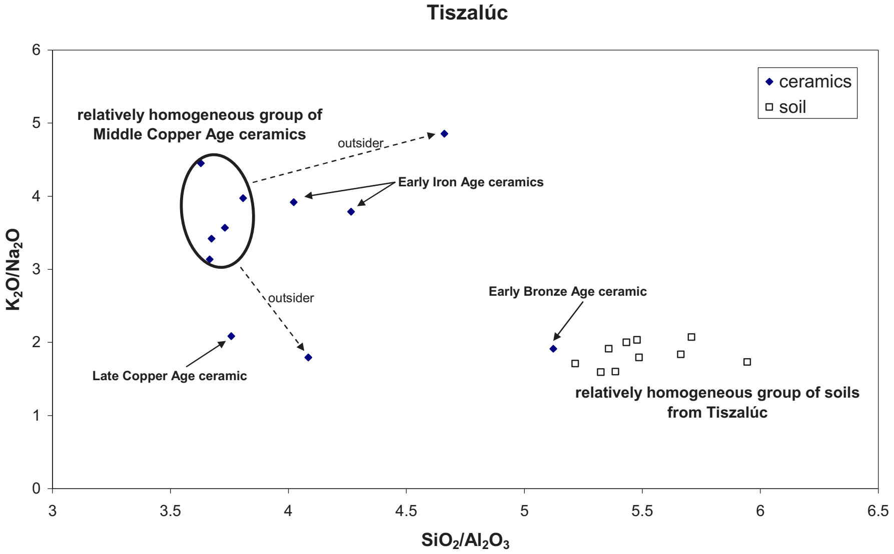

FIG. 9.4. *SiO_2/Al_2O_3 versus K_2O/Na_2O ratios for sediments and ceramics from the Tiszalúc region (in Hungary).*

distribution, we can generally state that the dominantly represented Middle Copper Age pottery forms a relatively homogeneous group with only a few outliers. The deviations are due to the elevated amount of volcanic components in the case of the outsider ceramics [9.7]. However, samples from the later periods can be clearly distinguished from the Middle Copper Age ones. On the basis of the limited number of measurements, the only suggestion of local raw material usage is that local raw materials were most probably used during the Early Bronze Age at Tiszalúc.

In addition to the primary concentration data, the XLSTAT 4.4 freeware program was used to apply statistical methods to the experimental data set. First of all, a principal component analysis (PCA) was run to transform the original concentration data to principal components (PCs).

As the outcome of these studies, we were able to contribute to the research on Neolithic pottery production in Vörs with the following observations: the ceramic material types and natural soil/sediment groups (Fig. 9.5) could be distinguished in a similar way as by the TiO_2/Al_2O_3 versus Zr/V bivariate correlation diagram (Fig. 9.2). However, there is a possibility of a different interpretation of the relationship of the archaeological ceramics and the clay source at Battyánpuszta. In contrast to the incompatible element ratio plot, this PCA observed exclusively the major element concentrations from the data set. PC1 involved Si and Mg with a weighted proportion, while PC2 calculated primarily with Al, Ti, Fe, K and Ca (which are partly immobile and incompatible, partly mobile, elements). This difference resulted in a stronger divergence of the Battyánpuszta source from both of the ceramic groups. Nevertheless, this type of raw material is still more probable for ‘carbonate sand tempered’ ceramics than for the ‘crushed pottery tempered’ ones.

9.5. CONCLUSIONS

Archaeological ceramics can be described as complex, artificially modified, natural materials (sediments). Their provenance investigations can be successfully carried out utilizing PGAA combined with other chemical methods (XRF and INAA). Considering the geochemical behaviour of the elements in partly natural (geochemical) and partly artificial (manufacturing) processes, it was possible to characterize chemically both the archaeological ceramics and the potential raw materials collected from the surroundings of the archaeological sites.

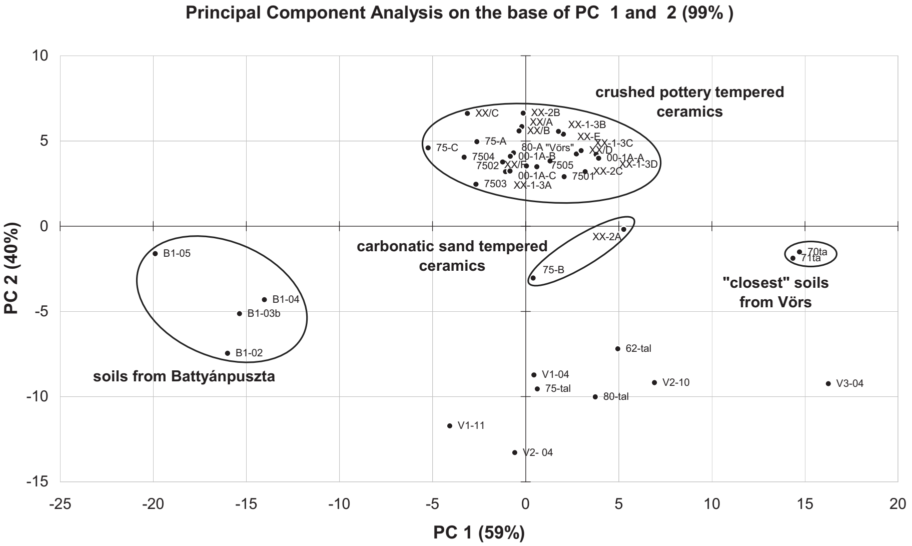

FIG. 9.5. Principal component analysis of sediments and ceramics composition data from the Vörs region (in Hungary).

ACKNOWLEDGEMENTS TO CHAPTER 9

We are very grateful for the support of the IAEA under CRP No. F23023 between 2004 and 2008.

We acknowledge the technical support of the Budapest Neutron Centre for the PGAA experiments. We thank M. Balla (Institute of Nuclear Techniques, University of Technology and Economics, Budapest) for the INAA measurements and H. Taubald (Tübingen University, Germany) for the XRF measurements.

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Chapter 10

CHEMICAL IDENTIFICATION OF ARCHAEOLOGICAL OBSIDIAN FROM LAGARTERO, CHIAPAS, MEXICO, USING MAIN AND TRACE ELEMENTS DETERMINED BY PIXE

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Abstract

Proton induced X ray emission (proton PIXE) analysis has been used for determination of minor and trace element concentrations of archaeological obsidian samples, which were collected at the site at Lagartero, Chiapas, Mexico. Samples of Mexican and Guatemalan sources were also analysed. Statistical treatments such as principal component analyses were applied to the data set. Obsidians from Lagartero were identified as coming from the Guatemalan sources of Ixtepeque and El Chayal, with one sample from Ucareo/Zinapécuaro, Mexico. These results indicate that there was contact between the population of Lagartero and other Mayans or Mesoamericans.

10.1. INTRODUCTION

The archaeological site of Lagartero (Chiapas, Mexico) is mainly a Classic Period Mayan site on the present day border between Mexico and Guatemala (Fig. 10.1), unique with a particular ecological environment in the Upper Grijalva Basin (UGB), presumably because it is surrounded by swamps which cover

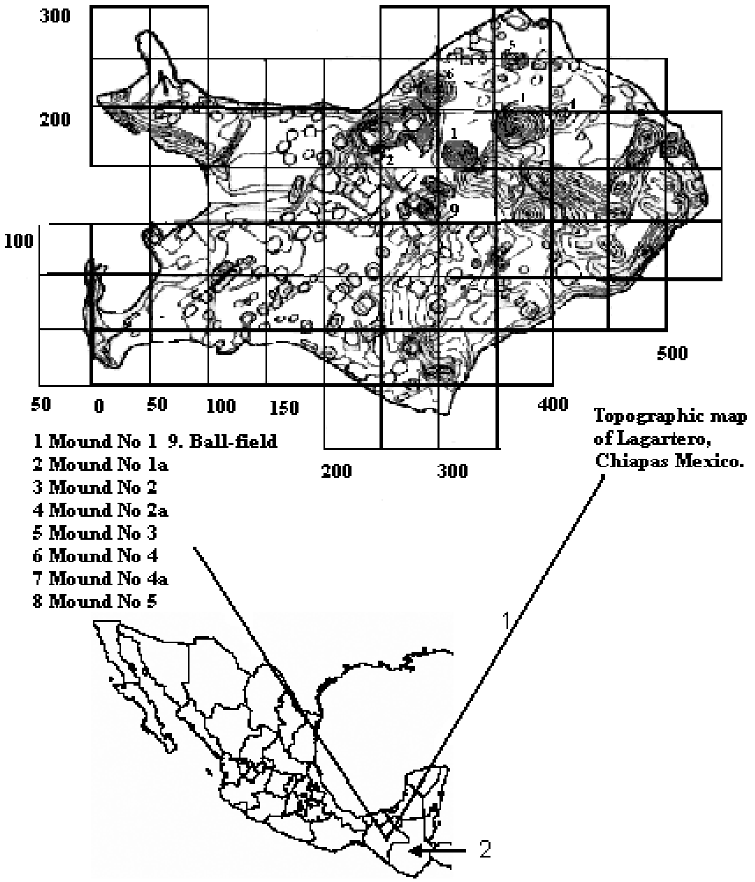

FIG. 10.1. Topographic map of the Lagartero region: (1) Chiapas, (2) Guatemala.

8.6 km^2 of swiftly flowing streams and lakes (Lagos de Colón) [10.1] fed by springs and the backed-up water of the Lagartero and San Lucas rivers diverted by natural travertine barriers. This archaeological site is the largest archaeological site of the upper Grijalva river basin, having a characteristic architectural style that has so far been well preserved.

According to the typology of the ceramic, this site was inhabited from the Protoclassical period (100 B.C.) to the Early Postclassical (A.D. 1200) period. It is thus an ideal place for the study of the process of cultural changes that took place over a period of 1300 years, involving both ceremonial and domestic aspects.

The site of Lagartero is composed of eight islands and seven peninsulas of different sizes. The largest island is called El Limonar, where most of the main and largest structures have been found. During the first field work, the whole island was divided into eleven units. Unit VII corresponds to the ball-field area, which before being excavated looked like two large parallel elongated mounds, one of which is 27.60 m long and 13.10 m wide, and the other of which is 27 m long and 13 m wide, both of them being 2.70 m high. When excavated, these mounds revealed two parallel structures which form the ball-field [10.1]. The obsidian samples chosen for this research came from this zone and had been obtained by a surface search within an area of 2024 m^2, before any specific deep excavations were carried out [10.2].

Among the pieces recovered, the obsidian devices are of special interest because of the political and religious importance of this material in pre-Hispanic times. The characterization of the most important obsidian sources and the identification of the origin of the devices found at the archaeological sites are essential in the reconstruction of the obsidian trade routes, which at times covered long distances, thus increasing, in great measure, the development of societies and their cultural exchanges.

The aim of the present research was to identify, by means of proton induced X ray emission (PIXE) and statistical methods, the origin of twenty samples, which were eleven debitage pieces and nine prismatic blade fragments with unpolished surfaces.

10.2. EXPERIMENTAL APPROACH

The analysed obsidian samples from Lagartero are described in Table 10.1. Samples of Mexican sources from Ucareo and Zinapécuaro (Michoacan) and one sample purchased in a workshop at Guaytán in Guatemala were analysed as well. All these samples were carefully brushed in order to eliminate dust; later on, after they had been washed by ultrasonic agitation using a 10% EXTRAN solution (Merck Co.) in distilled water, they were dried at environmental temperature.

The obsidian samples were analysed by PIXE using the AGLAE facility of the Centre de Recherche et de Restauration des Musées de France. The PIXE set-up is based on an external microbeam. The proton beam of 3 MeV and 2 μA is extracted in air through a 0.1 μm thick Si_3N_4 foil and focused with a diameter of 30 μm on the target with a triplet of magnetic quadrupole lenses. Two X ray detectors were used for simultaneous detection of matrix and trace elements. A first detector with an ultra-thin window and helium gas flushed along the path from target to crystal permits the determination of light elements ($10 < Z < 27$), which are the major constituents of the obsidian samples.

TABLE 10.1. ARCHAEOLOGICAL OBSIDIAN SAMPLES FROM LAGARTERO, CHIAPAS, MEXICO
(CG, El Chayal, Guatemala; IG, Ixtepeque volcano, Guatemala; U-Z, Ucareo-Zinapécuaro, Mexico)

Sample	Description/colour	Source
O1	Debitage pièce/Dark grey	CG
O2	Debitage pièce/Dark grey	CG
O3	Debitage light/Opaque grey	CG
O4	Debitage pièce/Dark grey	CG
O5	Blade fragment, medial part/Black	CG
O6	Blade fragment, distal part/Opaque light grey	CG
O7	Debitage pièce/Opaque striped light grey	CG
O8	Debitage pièce/Light grey	CG
O9	Blade fragment, proximal part/Striped light grey	U-Z
O10	Blade fragment, proximal part/Striped light grey	CG
O11	Debitage pièce/Translucent rosy grey	IG
O12	Blade fragment, medial part/Striped dark grey	CG
O13	Debitage pièce/Striped dark grey	CG
O14	Blade fragment, medial part/Striped dark grey	IG
O15	Debitage pièce/Gray with dark and light stripes	CG
O16	Debitage pièce/Translucent light grey	IG
O17	Debitage pièce/Translucent striped grey	CG
O18	Blade fragment, distal part/Opaque dark grey	CG
O19	Blade fragment, medial part/Striped dark grey	CG
O20	Blade fragment, medial part/Translucent striped dark grey	CG

Simultaneously, a second detector with a 50 μm aluminum filter is used for the measurement of trace element content ($Z > 26$). Element maps are carried out by moving the sample with a fixed beam with a motorized sample holder. Each obsidian sample was analysed at one or two points, depending on its size.

Quantitative analyses were obtained by processing two spectra, which were recorded at each spot with GUPIX software [10.3]. This computer code can conveniently provide major and trace element concentrations without measuring the integrated electric charge. The major constituents were extracted from the first spectrum only by normalizing the total oxide content to 100% without needing a dose of incident protons. The iron concentration delivered in the first step was subsequently used as an internal standard for the processing of the second spectrum to obtain the trace element content.

Chemical data were analysed using the MURR procedures for statistical analysis of multivariate archaeometric data written in the GAUSS language by H. Neff [10.4].

10.3. RESULTS

Seventeen elements were analysed by PIXE: Na, Mg, Al, Cl, K, Ca, Ti, V, Mn, Fe, Zn, Ga, Rb, Sr, Y, Zr and Nb; the results obtained are shown in Table 10.2. Statistical calculations were done taking into consideration the literature data [10.5–10.8] of the coincident elements (Na, Cl, K, Mn, Fe, Zn, Rb and Zr) of 30 obsidian sources. A good comparison was found. It is interesting to remark that concentrations of Al, Mg, Si, Ca, Ti, Ga, Sr, Y and Nb had not been previously reported for the obsidian samples of Zinapécuaro, Ucareo, El Chayal or the Ixtepeque volcano.

The dendrogram and principal component diagram (Figs 10.2 and 10.3, respectively) show an evident discrimination between the obsidian samples. Data for the Ucareo (UM) and Zinapécuaro (ZM) sources were obtained from the present research (Table 10.2), and those for El Chayal and Ixtepeque volcano and other data for ZM(l) and UM(l) were taken from the literature [10.5, 10.8].

The clusters in Figs 10.2 and 10.3 are the following: (a) sample 9, Ucareo and Zinapécuaro (Michoacan, Mexico); (b) samples 1, 2, 4–7, 10, 12, 13, 17–19, one purchased in a workshop in Guaytán and El Chayal (Guatemala); (c) samples 11, 14, 16 and Ixtepeque volcano (Guatemala). The elemental analyses of samples 3, 8 and 20 (Table 10.2) are similar to those of the cluster number 2; however, their chlorine contents are higher.

According to Table 10.2, the chemical composition of sample 9 is quite similar to the sample from Ucareo and differences are observed regarding the sample from Zinapécuaro, mainly for their chlorine and titanium concentrations. Therefore, this sample probably came from the Ucareo source, which had a considerable magnitude for exploitation and a truly pan-Mesoamerican importance in pre-Hispanic times [10.9]. Ucareo is located at 1100 km from Lagartero and it was probably reached by travelling along the Pacific coast, as was suggested for the obsidian found in the Lower Rio Verde Valley, Oaxaca [10.10].

TABLE 10.2. RESULTS OF THE PIXE ANALYSES OF ARCHAEOLOGICAL OBSIDIANS (O) FROM LAGARTERO, CHIAPAS, MEXICO

(Concentrations are in μg/g unless otherwise indicated. Individual data are grouped according to PC diagram and dendrogram: CG, El Chayal; IG, Ixtepeque volcano; G, Guaytán, Guatemala; U-Z, Ucareo-Zinapécuaro, Michoacán, Mexico.)

Element	O9 (U-Z)	Ucareo	Zinapécuaro	IG group *n* = 3[a]	CG group *n* = 14[b]	Sample G	O20	O3	O8
Na (%)	2.3	2.3 ± 0.2	2.7 ± 0.2	3 ± 1	2.7 ± 0.5	2.75 ± 0.04	2.9	3.2	4.3
Mg	503	350 ± 47	439 ± 63	1701 ± 72	1468 ± 298	2203 ± 644	1134	1348	1026
Al (%)	6.6	6.7 ± 0.02	6.63 ± 0.04	7.4 ± 0.2	7.1 ± 0.1	7.1 ± 0.06	7	7.3	6.6
Si (%)	36.1	35.92 ± 0.08	36 ± 0.06	34 ± 1	35.2 ± 0.8	35.22 ± 0.03	35.1	34.7	32.9
Cl (μg/g)	499	586 ± 64	831 ± 59	804 ± 55	794 ± 103	892 ± 110	2796	1729	1232
K (%)	4.1	4.2 ± 0.2	4 ± 0.1	3.9 ± 0.6	3.6 ± 0.5	4.2 ± 0.2	3.6	3.1	3.3
Ca (%)	0.4	0.4 ± 0.01	0.39 ± 0.03	0.87 ± 0.06	0.8 ± 0.07	0.8 ± 0.1	0.8	1.1	0.7
Ti (μg/g)	524	581 ± 60	360 ± 34	1565 ± 39	1141 ± 76	1346 ± 378	1180	1013	1039
Mn (μg/g)	198	205 ± 10	213 ± 26	527 ± 10	665 ± 62	638 ± 139	800	498	697
Fe (%)	0.9	1 ± 0.1	0.8 ± 0.1	1.04 ± 0.04	0.75 ± 0.09	0.9 ± 0.3	0.73	0.59	0.63
Zn (μg/g)	42	43 ± 4	47 ± 9	35 ± 4	41 ± 3	41 ± 4	49	37	38
Ga (μg/g)	23	19 ± 2	23 ± 2	17 ± 2	17 ± 2	17 ± 2	20	17	15

TABLE 10.2. RESULTS OF THE PIXE ANALYSES OF ARCHAEOLOGICAL OBSIDIANS (O) FROM LAGARTERO, CHIAPAS, MEXICO (cont.)

(Concentrations are in μg/g unless otherwise indicated. Individual data are grouped according to PC diagram and dendrogram: CG, El Chayal; IG, Ixtepeque volcano; G, Guaytán, Guatemala; U-Z, Ucareo-Zinapécuaro, Michoacán, Mexico.)

Element	O9 (U-Z)	Ucareo	Zinapécuaro	IG group $n = 3$[a]	CG group $n = 14$[b]	Sample G	O20	O3	O8
Rb (μg/g)	201	192 ± 16	237 ± 21	114 ± 5	146 ± 16	144 ± 41	175	112	154
Sr (μg/g)	19	21 ± 2	7 ± 2	171 ± 16	184 ± 25	162 ± 0.6	164	307	157
Y (μg/g)	22	28 ± 7	35 ± 6	20 ± 7	17 ± 4	18 ± 4	7	15	22
Zr (μg/g)	156	150 ± 19	123 ± 15	188 ± 12	121 ± 12	135 ± 33	118	103	108
Nb (μg/g)	19	18 ± 6	21 ± 5	12 ± 6	10 ± 4	18 ± 6	13	10	7

[a] Samples 11, 14 and 16.

[b] Samples 1, 2, 4–7, 10, 12, 13, 15, 17–19 and G.

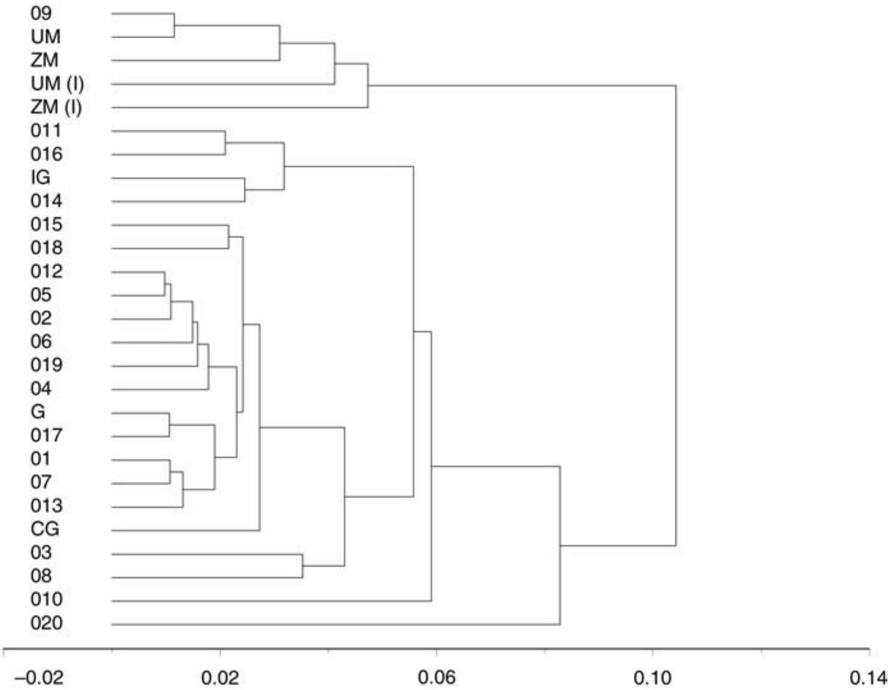

FIG. 10.2. Dendrogram for twenty obsidian samples from Lagartero, Chiapas, Mexico, one purchased in Guaytán, Guatemala (G) and the following sources: UM, Ucareo, Michoacán, Mexico; ZM, Zinapécuaro, Michoacán, Mexico. The data were taken from Cobean et al. [10.5] and Cobean [10.8] for: CG, El Chayal, Guatemala; IG, Ixtepeque volcano; UM(l) and ZM(l).

Cobean et al. [10.5] describe the flow from the Guatemalan sources at El Chayal as enormous, making it the most important obsidian source for lowland Maya centres during the Classical Period. The source at the Ixtepeque volcano is even larger than that at El Chayal, and its obsidian was widely traded all over southern Mesoamerica and lower Central America. Both sources are at a distance no further than 200 km from Lagartero as the crow flies.

The results of the present research indicate that 65% of the analysed samples of Lagartero came from El Chayal. This result is different from that found with an obsidian collection of artefacts from Chichén Itzá; in that case, the majority of them came from distant geological sources located in central and west Mexico, and only 10% came from El Chayal and 12% from Ixtepeque [10.11].

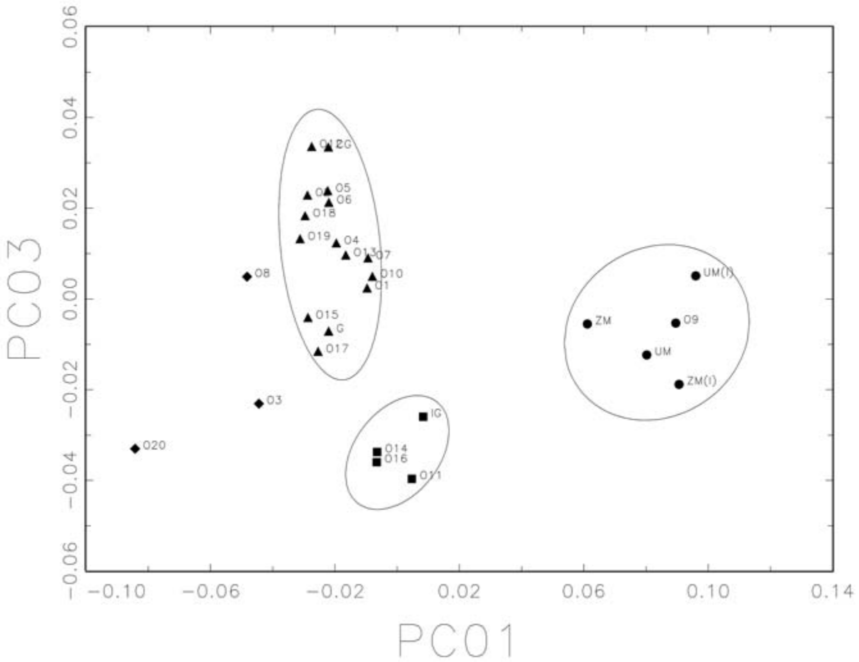

FIG. 10.3. Principal component diagram for twenty obsidian samples from Lagartero, Chiapas, Mexico, one purchased in Guaytán, Guatemala (G) and the following sources: UM, Ucareo, Michoacán, Mexico; ZM, Zinapécuaro, Michoacán, Mexico. The data were taken from Cobean et al. [10.5] and Cobean [10.8] for: CG, El Chayal, Guatemala; IG, Ixtepeque volcano, UM(l) and ZM(l). The confidence interval for the ellipses is 0.9.

10.4. CONCLUSIONS

The archaeological site of Lagartero is situated on a Mesozoic limestone substratum, and there are no igneous or metamorphic stones to be found anywhere in the vicinity. Therefore, the obsidian used was purchased from the nearest sources, for example, El Chayal and the Ixtepeque volcano. The raw material probably arrived by the barter of other goods or services, and it was probably brought to the site in nodules because of the evidence of obsidian workshops at Lagartero.

The blade fragment identified as coming from Ucareo shows that exchange took place over a long distance even though on a minor scale. That implied a long sweep of both distance and time. Owing to the small quantity found at the site, these materials probably did not arrive directly but passed through different hands and over several chronological periods.

Our results lead us to infer that the population of Lagartero certainly had contact with other Mayans and Mesoamericans.

ACKNOWLEDGEMENTS TO CHAPTER 10

This research is a part of the project, "Characterization of Archeological Pieces from Lagartero, Chiapas, Mexico" financed by the IAEA, Project No. 13070/RO. The technical assistance of J. Muñoz Lujano is much appreciated.

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CHAPTER 11

APPLICATIONS OF NUCLEAR ANALYTICAL TECHNIQUES TO INVESTIGATE THE AUTHENTICITY OF ART OBJECTS

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Abstract

One hundred and twenty-seven Nazca pottery and ten imitations were analysed by thermoluminescence, neutron activation analysis, X ray fluorescence, transmission electron microscopy, X ray diffraction and Mössbauer spectroscopy, to obtain analytical differences that allow differentiating them quickly. Additionally, 20 pieces of the Wari culture found in the city of Cahuachi were analysed. The multielementary composition of the Nazca ceramics obtained by AAN allows, owing to a multivariate analysis, differentiation of the samples according to their geographic origin but a chronological classification could not be obtained. This indicates that the Nazca pottery of each city was always prepared with the same raw material. However, samples from the museum of the UNMSM could not be classified, since these samples were collected in all Nazca regions. The brown, orange and yellow pigments of Nazca pottery contain different amounts of manganese and iron oxides. The same elements were found in modern ceramics, but additionally lead and zinc were detected in the yellow colour of modern ceramics. The presence of illita in the paste of all the analysed samples indicates that the firing temperature of Nazca pottery did not exceed 800°C. Also, the fact that the quadrupole splitting in the Mössbauer spectra as a function of temperature stays more or less constant until 700°C and soon falls quickly indicates that the firing temperature was approximately 700°C. This was corroborated with the same analysis on samples from modern ceramics heated to approximate temperatures of 700°C and 900°C.

11.1. INTRODUCTION

The Nazca culture was developed in the zone of the same name. This is a desert zone near the sea (Fig. 11.1). The main cities where important remains of this civilization have been found are Palpa, Cahuachi and Marcaya. Nazca ceramics are characterized by the use of several colours and their good finish, reasons that have inspired numerous craftworkers to imitate these archaeological pieces. The ceramics of this culture is divided by archaeologists into eight stylistic phases.

Initially, 60 samples originating from the Museum of Archaeology and Anthropology of the Universidad Nacional Mayor de San Marcos were analysed, and then 53 Nazca ceramic fragments from Palpa, 14 from Cahuachi, and 20 Wari culture ceramics found in the city of Cahuachi were also analysed.

These samples were analysed using themoluminescence (TL), neutron activation analysis (NAA), X ray fluorescence (XRF), transmission electron microscopy (TEM), X ray diffraction (XRD) and Mössbauer spectroscopy [11.1–11.5].

The Nazca ceramic imitations were acquired in Palpa, in the Segura workshop. Figures 11.2 and 11.3 show the Segura workshop and the furnace used there.

In addition, the same craftworker was asked to prepare sample trowels that all contain the colours used in the preparation of modern Nazca ceramics. Additionally, the Segura craftworker made three trowels: one without any heating and two others fired to approximately 700°C and 900°C (Fig. 11.4).

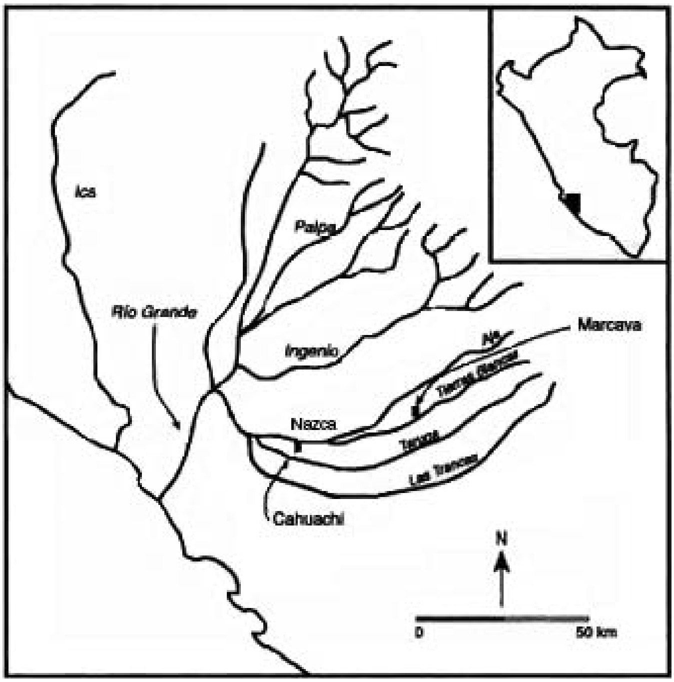

FIG. 11.1. Geographic zone of the Nazca region showing the cities of Palpa and Cahuachi.

FIG. 11.2. (a) Production of a modern ceramic and (b) the furnace at the Segura workshop.

FIG. 11.3. Materials used in the preparation of modern Nazca ceramics and a comparison of a modern ceramic with an original ceramic item.

FIG. 11.4. Trowel containing the different colours used by the Segura workshop, along with trowels without colours with different firing treatments.

11.2. RESULTS AND DISCUSSION

11.2.1. Authenticity experiments using thermoluminescence

Twenty fragments of Nazca pottery and three modern pieces have been analysed by thermoluminescence. In order to obtain the samples, a drill with a diamond reel was used. The samples were taken from a depth of 2 mm into the fragment. The measured values for samples from the museum do not show any chronological correlation, perhaps due to their long exposure to light. However, the modern samples did not present any residual luminescence signal. This test allows a quick differentiation between old ceramics and modern ones.

11.2.2. Paste analysis by light microscopy

The cross-sections of the fragments from Nazca pottery were cleaned and washed with distilled water, and dried with a lamp. The quality of the paste and the inclusion of additives were observed with a stereoscope of 20× magnification and with a digital camera. From the images, it was deduced that the Nazca potters included different additives in their ceramics. For example, in a ceramic from phase II, dark grains (0.1–0.5 mm diameter) and colourless grains are observed (probably quartz of 1 mm in diameter). However, in the ceramic from phase IV, dark grains of up to 3 mm diameter predominate. Samples from phase V present dark, fine grain agglomerates of 1 mm diameter, and an abundance of clear and dark grains of between 0.05 and 0.1 mm diameter. The paste of phase V looks very homogeneous with very low porosity. These characteristics and the fineness of the work demonstrate the high technical development of the potters. From phase VIII onwards, the presence of large inclusions is again observed, demonstrating that the paste is inhomogeneous, and showing little dominion by the potter.

11.2.3. Fragments classification using NAA data and multivariate analysis

One hundred and forty-seven samples have been analysed by NAA using the k_0 method. All the samples were irradiated with a reference material, Ohio Red Clay. For the multivariate analysis, the software MURR, Statistical Routine for Gaussian, developed in the University of Missouri, was used. A dendrogram was first obtained and then, after elimination of the outer layers, a principal components analysis allows classification of the samples from Palpa, Cahuachi and Wari into two groups. The samples from Palpa separate clearly from those from Cahuachi and Wari (Figs 11.5 and 11.6). However, it was not possible to obtain any classification with the data from the UNMSM museum samples. This indicates that it is not possible to obtain a chronological classification but only a geographic classification.

The main elements found in the paste are: K, Ca, Mn, Fe, Co, Sr, Y, Zr, Nb and Pb. These elements are also in the paste used in modern ceramics, but additionally arsenic is observed in the modern ones. The analysis by XRF of pigments allowed to identify the elements present in the colours brown (Mn, Fe and Zn), yellow (Ga and Fe), target (Ca, Mn and Zn), ochre (Fe and Ba) and orange (Fe, Zn, Rb and Sr). The same elements were found in pigments from modern ceramics. Nevertheless, for the colour yellow the presence of Zn and Pb in the modern ceramics was additionally observed.

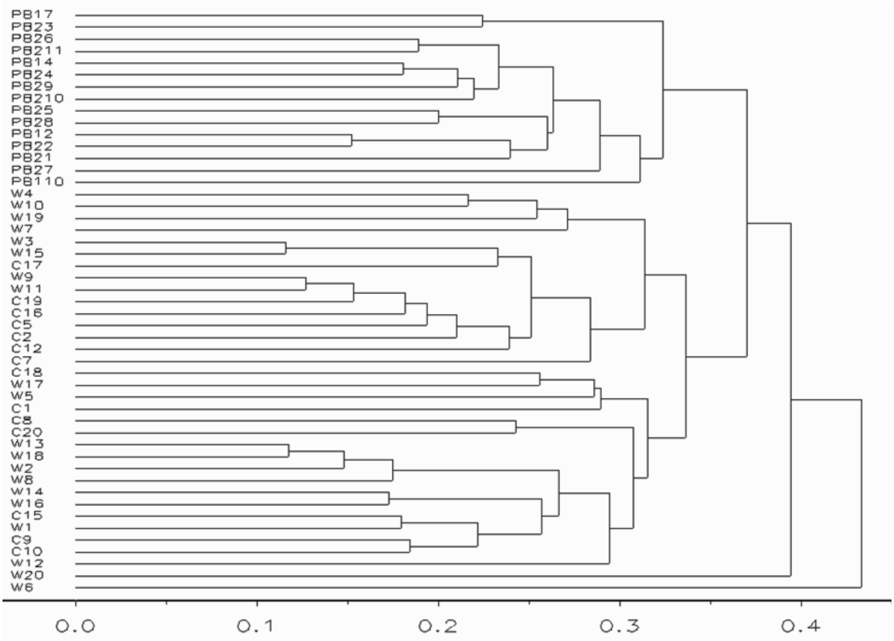

FIG. 11.5. Dendrogram obtained from data from Palpa, Cahuachi and Wari samples.

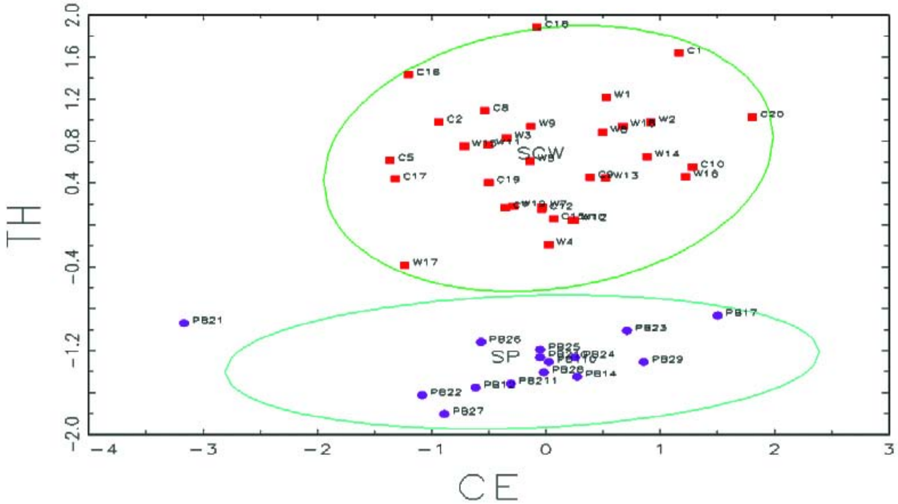

FIG. 11.6. Groups obtained from data from Palpa (P), Cahuachi and Wari (W) samples. Paste and pigment analysis by XRF.

11.3. MICROSTRUCTURAL STUDIES OF THE PASTE USING TEM

Electron diffraction patterns of selected areas of the paste were obtained. The interplanar distances of the crystalline components of the paste were determined and compared with the values in a database of diffraction distances. Different minerals, such as quartz and haematite, as well as clays Clay 239 and Clay 180, were identified. As expected, the results obtained by electron diffraction only show the crystalline components, without showing the amorphous components that might be present. However, the presence of illite in all the materials studied was observed. This is evidence that the firing temperature of the Nazca ceramic did not exceed 800°C, because illite mineral undergoes a chemical change above this temperature.

When analysing the pigments with a magnifying glass of 30×, it can be seen that the pigments are a mixture of several colours, with the pigment found in the largest amount predominating. In the colour black, we could observe also grey, brown, yellow and orange grains. Inclusively, magnetic dark particles were observed. These particles were easily separable with a magnet. This heterogeneity is comprehensible since potters in earlier times did not have techniques or knowledge of the pigment purification and homogenization.

Some samples exhibit zones with microfossil marks with diameters that are between 50 and 400 nm (the sample HPIM 4524-17), which were also observed in the reference material, Ohio Red Clay (Fig. 11.7).

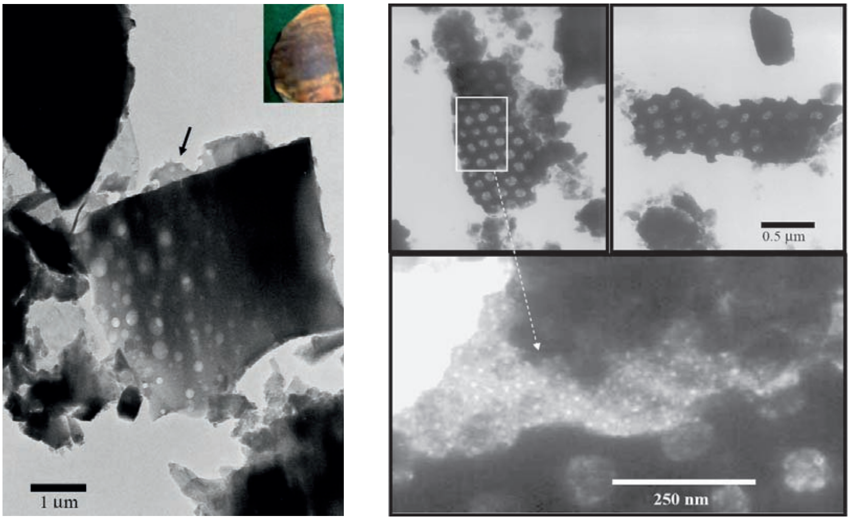
(a)
(b)

FIG. 11.7. Particles with microfossil marks found in (a) a Nazca fragment and (b) in a sample of the reference material, Ohio Red Clay.

11.4. FIRING TEMPERATURE DETERMINATION USING MÖSSBAUER SPECTROSCOPY

The Mössbauer spectra of the samples were analysed with the software PCMOS. This software determines all the paramagnetic contributions and found six curves, three of which present doublets and the other three are constituted of sextuplets. This same software calculates the contribution of the different iron species, there being a greater contribution of Fe(II) in dark samples.

In order to determine the firing temperature of the Nazca pottery, samples were heated to between 300–1000ºC with intervals of 100ºC, in an oxidant atmosphere for 12 hours. The Mössbauer spectrum was taken from the sample after cooling. The relative areas of the paramagnetic sites, and their respective quadrupole splitting average, were determined for each temperature. These values remain almost constant with the thermal treatment of the samples until 700ºC, and then these values increase for higher temperatures (Fig. 11.8), indicating the original firing temperature was around 700ºC. This is based on the fact that the hyperfine parameters that characterize the structural order of the material in a study must remain fixed until the original firing temperature has been surpassed.

The presence of a doublet from Fe(II) that persists until 950ºC can be due to the presence of muscovite in the paste. This doublet disappears after reaching 1000ºC, indicating that the muscovite mineral undergoes a chemical change.

In order to validate the experiment, three modern trowels were made with the same raw material: one did not receive any thermal treatment and two were fired to the temperature T_1 (approximately 700ºC) and T_2 (approximately 900ºC). The Mössbauer spectra of these samples were very different (Fig. 11.9). This indicates to us that the temperature reached during the thermal treatment has produced irreversible chemical changes in the raw materials which depend on the firing temperature, and that the Mössbauer spectra show the magnetic characteristics of these materials.

To determine the firing temperature of the sample heated to temperature T_1, a sample of this piece was heated to 450, 500 and 800°C for 12 hours. The Mössbauer spectrum of the samples heated to 450 and 500°C were similar, but one of the samples heated to 800°C was very different from the previous one but identical to the sample fired to the temperature T_2 (Fig. 11.10). Because we do not yet have data at intermediate temperatures, it is deduced that the firing temperature T_1 is between 500 and 800°C. Also, it is deduced that the temperature T_2 must be higher than 800°C.

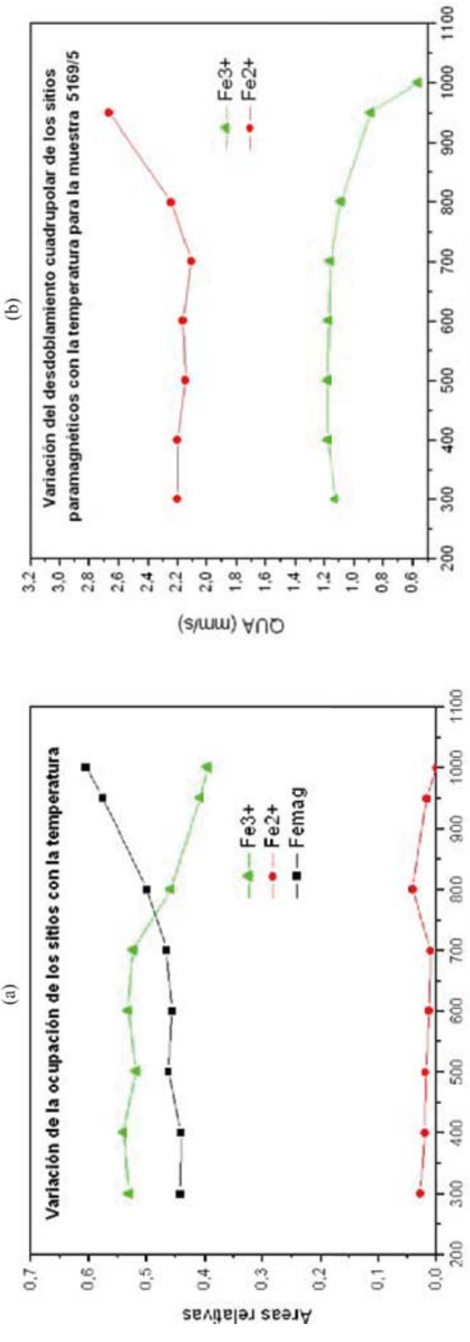

FIG. 11.8. Variation for the sample Nazca III–5169/5 of (a) the occupation of the iron sites and (b) the quadrupole splitting with the temperature.

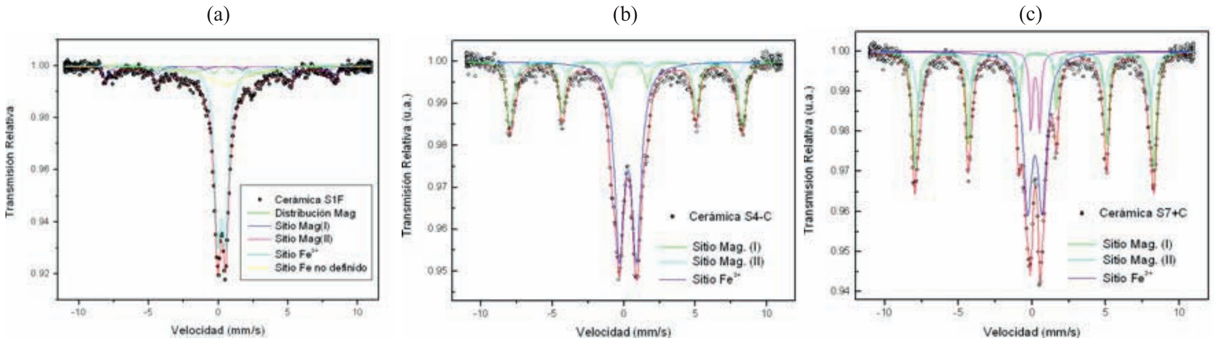

FIG. 11.9. Mössbauer spectra of the samples: (a) without thermal treatment, and fired to (b) temperature T_1 and (c) temperature T_2.

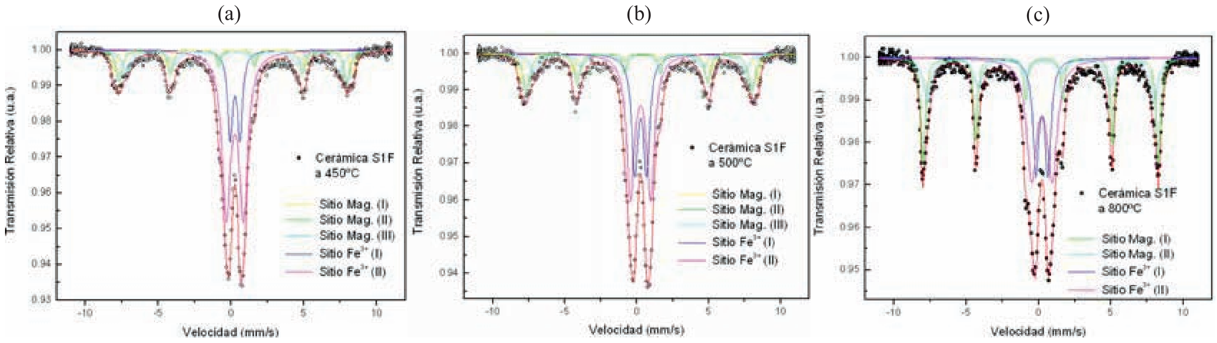

FIG. 11.10. Mössbauer spectra of the sample fired at the temperature T_1, treated at (a) 450°C, (b) 500°C and (c) 800°C.

11.5. CONCLUSIONS

The data collected by thermoluminescence did not allow differentiating the samples chronologically. This is perhaps explained by the fact that the samples studied came from the UNMSM museum, and had been continuously exposed to light, which modifies the variable that is measured. Therefore, this technique is not adaptable to obtain a chronological classification of the Nazca ceramics, but allows a clear differentiation from its imitations.

The multielementary composition of the Nazca ceramic obtained by NAA allows, by means of the multivariate analysis, a geographical classification of the samples. This indicates that the Nazca ceramic of each city was always prepared with the same raw material. However, the statistical analysis of data from the UNMSM museum did not allow a classification.

The analysis of the paste by optical microscopy allows determining the advancement of the technical potter throughout the different stylistic phases of the Nazca ceramics. On the basis of the grain size and uniformity of the paste, we concluded that the Nazca potters reached a higher level of their technique during phase V.

According to the XRF data from pigments, the brown, orange and yellow pigments contain different amounts of manganese and iron oxides. The same elements were found in modern ceramics, but additionally lead and zinc were detected in the yellow colour of the modern ceramics. Nevertheless, the white colour shows the presence of calcium, perhaps in carbonate form.

The analysis of the electron diffraction patterns obtained by TEM did not allow classifying the analysed ceramics. However, the presence of the mineral illite in all the studied fragments was determined. Considering that illite is transformed completely into another species when it is heated over 800°C, we can deduce that the firing temperature of the Nazca ceramics did not exceed this temperature.

New evidence on the firing temperature was obtained using Mössbauer spectroscopy. Indeed, the measurement of the quadrupole splitting as a function of the temperature remains more or less constant until 700°C and then falls quickly. This indicates that the firing temperature was approximately 700°C. This was corroborated with similar experiments performed with modern ceramics, which were fired at two temperatures, 700°C and 900°C.

Additionally, the presence of a doublet from the contribution of Fe(II) for the Nazca ceramics with a thermal treatment under 1000°C due to the presence of muscovite indicates that this mineral undergoes a chemical change at this temperature.

ACKNOWLEDGEMENT TO CHAPTER 11

The authors are grateful to the IAEA for the partial financing of this project (Project No. PER 13058).

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Produced by the IAEA
in Austria, September 2011

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