Application of Chemistry in Archaeology

ومن يؤت الحكمة
فقد اوتى خيرا كثيرا

QUAID-I-AZAM UNIVERSITY
ISLAMABAD

By

Abdul Basit

Research Supervisor

Dr. Ghani-ur-Rahman

Taxila Institute of Asian Civilizations

Quaid-i-Azam University

Islamabad

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Candidate's Declaration

I hereby declare that this thesis is the result of my individual research, and that it has not been submitted concurrently to any other university for any degree.

A. Basit

Abdul Basit

Taxila Institute of Asian Civilizations

Quaid-i-Azam University, Islamabad

I hereby recommended that the dissertation prepared under my supervision by **Mr. Abdul Basit**, titled: "**Application of Chemistry in Archaeology**", be accepted in partial fulfillment of the requirement for the degree of Master of Science in Archaeology.

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Dr. Ghani-ur-Rahman

Assistant Professor

TIAC, QAU

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TIAC, QAU

QUAID-i-AZAM UNIVERSITY

Taxila Institute of Asian Civilizations

Dated: 05-08-2014

FINAL APPROVAL

This is to certify that we have read the thesis submitted by **Abdul Basit** and it is our judgment that this thesis is of sufficient standard to warrant its acceptance by the Quaid-i-Azam University, Islamabad, for the award of degree of Master of Science in Archaeology.

Supervisor: ____________________

Dr. Ghani-ur-Rahman

Examiner: ____________________

Dr. Ijlal Hussain Shah

Director: ____________________

Prof. Dr. M. Ashraf Khan

Dedicated to my parents and grandfather Raza Khan

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Abbreviations

OES	Optical Emission Spectroscopy
AAS	Atomic Absorption Spectroscopy
ICP	Inductively Coupled Plasma Atomic Emission Spectroscopy
XRF	X-ray Fluorescence
TLC	Thin Layer chromatography
GC	Gas chromatography
HPLC	High Performance Liquid Chromatography
TIMS	Thermal Ionization Mass Spectrometry
SEM	Scanning Electron Microscopy

Contents

Introduction

Chemistry is the study of the elements and the compounds. These are formed when they bond with each other. There are three main branches of chemistry: Physical chemistry, inorganic chemistry, and organic chemistry. Physical chemistry is the branch of chemistry, which deals with the physical properties and physical behavior of material things. It includes the study of chemical bonding and the structure of solids, liquids and gases. Inorganic chemistry is the study of all elements and their compounds, except compounds of carbon. Organic chemistry is the branch of chemistry in which we study the compounds of carbon. There are also related branches of chemistry such as biochemistry, analytical chemistry, industrial chemistry, chemical engineering, and geochemistry (Clugston and Flemming 2000: 12).

The earliest uses of chemical processes were in the extraction of metals such as copper and iron, the firing of clays and sands to make ceramics and glasses, and the extraction and use of dyes. People were able to do all these things, but how could they explain what they saw happening? When thinking about the material world, people have always tried to find patterns and describe rules of behavior. At first in the fifth century BC, their sorting was very broad. They concluded that there were four main categories of substance: fire, air, water, and earth. Each of these four categories was composed of pairs of the four fundamental qualities: hot, cold, wet, and dry. Everything in the whole of non-living world had to fit one of these categories or a combination of them (Clugston and Flemming 2000:13).

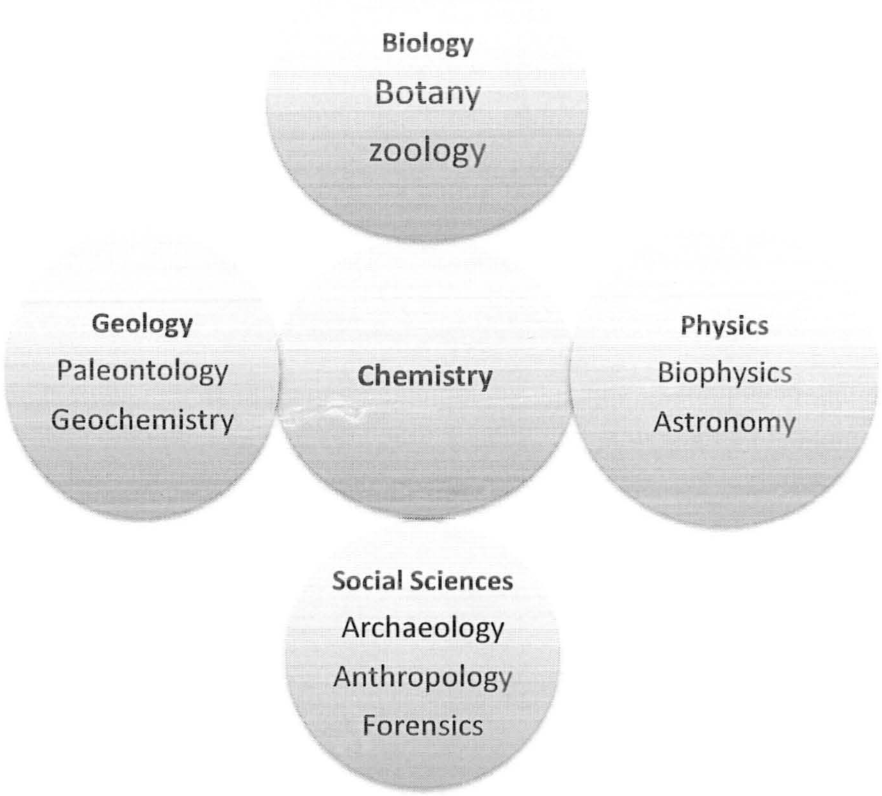

Figure 1: the Relationship between Chemistry and Other Sciences (Skoog et al. 2011: 5)

At a simple level this classification works: mountains, deserts, rocks, and houses are all 'earthy'; all liquids are watery; all gases are airy; and all flames are fiery. This scheme can also explain changes in materials. The systematic study of chemistry as a subject started in Egypt about 1700 years ago. Writings by Zosimos (c.AD 300) describe chemical experiments and chemical apparatus. For the next thousands years, most chemical exploration sought ways of changing cheap base metals such as lead into the precious metals, gold or silver. This work on transmutation was called *alchemy*. They did not succeed in their search but, almost accidently, they developed many sound techniques of chemical manipulation. Modern chemistry was born during the seventeenth century when some of these early scientists started to investigate the mechanism by which substances were changed. During the seventeenth century the study of chemistry began to concentrate on the preparation, isolation and use of new substances. In 1661, Robert Boyle wrote a landmark book called *The Sceptical Chymist*, in which he attacked the idea of four categories and introduced the modern concept of chemical elements. During the following two centuries Boyle's ideas took root and slowly developed. In 1789, in his *Elementary Treatise on Chemistry*, Antoine Lavoisier published a list of 33 chemical elements, many of which we recognize today. At that time an element was thought of as a substance that cannot be broken down into two or more simpler substances. We know now that an element is a substance that contains only one sort of atom, and that an atom is the smallest particle of an element that can exist independently. Most of our modern chemical understanding rests on these two simple and fundamental points (Clugston and Flemming 2000:13).

Chemistry has important practical applications in explaining our material world. Chemistry figures prominently in other fields (Ebbing et al.2009:2). Chemistry is often called the central science (Skoog et al. 2011: 4). Therefore chemistry has also great applications in archaeology. Modern archaeological research involves collaboration of archaeologists and natural scientists. To understand the material remains of past societies, archaeology has interacted more and more with the sciences of physics, chemistry, and biology and earth science. Among scientific disciplines chemistry is more closely associated with archaeology. Humans have always used chemicals and experienced chemical activity, and developed chemical process. All materials are either chemical substances or mixtures of chemical substances. Thus chemicals have always been part of the human experience (Goffer 2007: xvii).

Archaeology requires understanding of the chemical nature and properties of archaeological materials. The application of chemical methods to archaeology is called "archaeological chemistry". Today archaeological chemistry identify ancient materials and also makes it possible to understand how and when materials were worked, altered or manufactured, to find out their provenance, and trace the routes along which they were transported and traded (Goffer 2007: xvii).

Archaeological chemistry is primarily concerned with measuring the chemical composition of a variety of archaeological materials. Information on identity and composition is used for authentication, conversation and answering archaeological questions about the past (Price and Burton 2011:2).

These studies can tell us about subsistence and diet, exchange and trade, residence, demography, status, and many other aspects of prehistoric human behavior and activity. Chemical analysis is used for the detection and quantification of the inorganic elements, but also includes methods of organic analysis, and more recently techniques for the measurement of isotopic abundances for a range of elements (Price and Burton 2011:3).

The long history of the relationship between archaeology and chemistry deals with the use of chemistry to identify the constituents of archaeological artifacts. In chemistry there is a great contribution of great scientists such as Martin Heinrich Klaproth (1743– 1817), and they used archaeological materials for study. As a pharmacist, Klaproth devoted himself to the chemical analysis of minerals from all over the world. He discovered three new elements – uranium, zirconium, and cerium – and named the elements titanium, strontium, and tellurium, isolated by others but sent to him for confirmation. In addition to these great contributions to mineralogical chemistry, Klaproth determined gravimetrically the approximate composition of six Greek and nine Roman copper alloy coins, a number of other metal objects, and a few pieces of Roman glass. Gravimetry is the determination of an element through the measurement of the weight of an insoluble product of a definite chemical reaction involving that element, and was the principal tool of quantitative analytical chemistry until the development of instrumental techniques in the early twentieth century. Humphry Davy (1778–1829), discoverer of nitrous oxide (N_2O, or ''laughing gas'', used as a dental anesthetic and today as a general pain-killer), identifier of the chemical nature of chlorine gas, and inventor of the miner's safety lamp, also played a part in developing archaeological chemistry. In 1815, he read a paper to the Royal Society concerning the chemical analysis of ancient pigments collected by himself in ''the ruins of the baths of Livia, and the remains of other palaces and baths of ancient Rome, and in the ruins of Pompeii''. In a series of letters reported by others in the journal *Archaeologia*, Michael Faraday (1791–1867), the discoverer of electromagnetic induction, showed that he had studied a wide range of archaeological material, including a copper alloy coin, glass, and various fluids, enameled bronze, glass, fuel residue, food residue, and oil and Roman lead glaze pottery. One of the first wet chemical investigations of ancient ceramics (Athenian pottery from the Boston Museum of Fine Arts) was carried out at Harvard and published in the American Chemical Journal by Theodore William Richards (1895). Many other eminent chemists of the nineteenth century, including Kekule, Berzelius, and Berthelot, all contributed to the growing knowledge of the chemical composition of ancient materials. Their archaeological interests were minor compared to their overall contribution to chemistry, but these great scientists included the analysis of archaeological objects as part of their process of discovery. Later then systematic collaboration between archaeology and chemistry appeared. Examples include the analysis of four Assyrian bronzes and a sample of glass in Austen Henry Layard's Discoveries in the Ruins of Nineveh and Babylon (1853), and Heinrich Schliemann's Mycenae (1878). William Gladstone, the British Prime Minister of the day, wrote the preface. The scientific reports in both of these publications were overseen by John Percy (1817–89), a metallurgist at the Royal School of Mines in London. Percy also wrote four major volumes on metallurgy, which included significant sections on the early production and use of metals. Toward the end of the nineteenth century, chemical analyses became more common in excavation reports, and new questions, began to be asked. In 1892, Carnot published a series of three papers that suggested that flourine uptake in buried bone might be used to provide an indication of the age of the bone. Fluorine uptake was heavily relied upon, together with the determination of increased uranium and decreased nitrogen. This methodology became known as the ''FUN method of dating'' (flourine, uranium, and nitrogen) when applied to fossil bone. The development of instrumental measurement techniques during the 1920s and 1930s such as optical emission spectroscopy gave new analytical methods, which were applied to archaeological chemistry. The principal research aim at the time was to understand the technology of ancient bronze metalwork, especially in terms of identifying the sequence of alloys used during the European Bronze Age. Huge programs of metal analyses were initiated in Britain and Germany. As a result of the rapid scientific and technological advances precipitated by the Second World War, the immediate postwar years witnessed a wider range of analytical techniques being deployed in the study of the past, including X-ray analysis and electron microscopy, neutron activation analysis, and mass spectrometry. Materials other than metal, such as faience beads and ceramics, were subjected to large-scale analytical programs. Faience, an artificial high temperature siliceous material, was first produced in the Near East, and during the second millennium B.C it was distributed widely across prehistoric Europe as far as England and Scotland. In 1956, Stone and Thomas used OES to ''find some trace element, existent only in minute quantities, which might serve to distinguish between the quartz or sand and the alkalis used in the manufacture of faience and glassy faience in Egypt and in specimens found elsewhere in Europe''. This study represents a clear example of the use of chemical criteria to establish provenance: to determine whether faience beads recovered from sites in Britain were of local manufacture, or imported from Egypt or the eastern Mediterranean. This question was of great archaeological significance, because for many years it had generally been assumed that significant technological innovations originated in the east and had diffused westwards – a theory termed infusionism in archaeological literature. Although the initial OES results were equivocal, the data were subsequently reevaluated by Newton and Renfrew (1970), who suggested a local origin for the beads on the basis of the levels of tin, aluminium, and magnesium. This conclusion was supported by a subsequent reanalysis of most of the beads using neutron activation analysis (NAA) by Aspinall et al. (1972). During the late 1950s and early 1960s, the infusionist archaeological philosophies of the 1930s were replaced by radical new theoretical approaches in anthropology and the social sciences. This became known as ''New Archaeology'', and represented an explicit effort to explain past human action rather than simply to describe it. The philosophy of science played a significant role in providing the terminology for this more statistical and quantitative approach to archaeology. The movement of population, via invasion or diffusion of peoples, was no longer seen as the principal instigator of cultural change. Instead, internal processes within society were emphasized, although evidence for ''contact'' arising from exchange of artifacts and natural materials was seen as an important factor and one in which chemical analysis of artifacts and raw materials might be useful. This increased interest in the distribution of materials initiated a ''golden era'' in archaeometry as a wide range of scientific techniques were employed in the hope of chemically characterizing certain rock types, such as obsidian and marble, as well as ceramics, metals, glass, and natural materials, such as amber. These characterization studies were aimed at ''the documentation of culture contact on the basis of hard evidence, rather than on supposed similarities of form''.

Quantitative chemical data formed part of the basis of this ''hard evidence'', which made it necessary for archaeologists to become familiar with the tools and practice of chemistry, as well as the quantitative manipulation of large amounts of analytical data. Until recently, the applications of chemistry to archaeology focused primarily on inorganic artifacts – the most obviously durable objects in the archaeological record – or occasionally on geological organic materials such as amber and jet. Increasing attention has been directed over the past few decades towards biological materials – starting with natural products such as waxes and resins, but extending to accidental survivals such as food residues, and, above all, human remains, including bone, protein, lipids, and, most recently of all, DNA. The preservation of a wide range of biomolecules has now been demonstrated in a number of archaeological contexts (Pollard et al. 2007:5-10).

Other applications of chemistry to archaeology include Optical Emission Spectroscopy (OES), Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Optical and UV Spectrophotometry, Infrared Absorption Spectroscopy, Raman Spectroscopy, X-ray Fluorescence Spectrometry (XRF), Electron Microscopy, X-ray Diffraction, Chromatography and Mass Spectrometry. These analytical methods can be used to study archaeological materials. The concerned report deals with the application of chemistry in archaeology. It also includes all the analytical methods of chemistry which can be used in archaeology (Pollard et al. 2007:5-10).

The research under the title of "application of chemistry in archaeology" deals with the modern applications of chemistry in archaeology. The researcher has applied Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and X-Radiography to analyze the archaeological materials of District Shangla, Pakistan[1]. The research is also a comparative analysis of chemistry and archaeology with the indication of how facts, methods and theories of chemistry can be applied to the field of archaeology.

Statement of Problem

Archaeology yields information and develops theories about past human activity by means of a study of ancient materials remains. Important archaeological information can be obtained by the investigations of chemistry of the material remains. Therefore chemistry skills are central to archaeological investigations. But there is no such surprising combination of chemistry and archaeology to reduce the traditional way of human past study. There are a lot of weaknesses in traditional process of human past study and due to which numerous significant archaeological information could not be obtained. Published work about application of chemistry in archaeology is scattered in nature or not enough therefore much more work remains to be done. The application of chemistry to archaeology requires a remarkable degree of interaction between chemists and archaeologists. In fact, at present in Pakistan there are very few chemists who have a complete background in archaeology. On the other hand, most professionals involved with archaeology have a purely archaeological or artistic background, but often with no knowledge of the principles and techniques of chemistry. The traditional academic separation between chemistry and archaeology in higher education has restricted the mutual collaboration of these two disciplines. In Pakistan there are no laboratories associated with museums and archaeological institutions, or institutions dedicated to technical conservation. Frequently research on archaeology is carried out on a rare basis by chemists. They happen to work in archaeology for a limited amount of time, and then return to their main field. To overcome these

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[1] The archaeological samples for the chemical analysis of this study are provided kindly by Dr. Ghani-ur-Rahman from the archaeological data he has collected during his survey and documentation of District Shangla.

problems a mutual overlap of chemistry and archaeology is required to place archaeology as a modern science.

Hypothesis

The application of chemistry will bring revolution in the field of archaeology and it will convert traditional archaeology into "Revolutionized Scientific Archaeology".

Significance of Study

The research will focus on the interdisciplinary collaboration between chemistry and archaeology. It will form a more coherent bond between these two disciplines. This cross-disciplinary research will place archaeology in the modern sciences. Additionally the Significance and scope of this research is that:

- Application of chemistry will provide archaeology with absolute measurement of the chemical composition of a variety of archaeological materials. The chemical composition will identify the archaeological material. Chemical composition of archaeological materials can be used for different purposes like authentication, conservation, and answering archaeological questions about the past.
- The researcher has used X-Ray Diffraction for the analysis of archaeological materials. XRD is an extremely powerful tool because it is the most straightforward instrumental technique for identifying crystalline phases of archaeological material. The combination of traditional mineralogical and petrological tools in the physicochemical characterization of materials is essential in the modern investigation of complex archaeometric materials.
- With the use of X-Radiography it is easy to appreciate why radiography is being used more and more in the study of archaeological and cultural objects. It is proficient of

answering many questions about function, manufacture and state of preservation, sometimes providing information that is unavailable by another technique.

- SEM (Scanning Electron Microscope) can be used for the measurement of elemental composition of materials under analysis. The researcher has used SEM to combine visual and chemical capabilities in a single instrument. Thus it is the most modern analytical technique applied in archaeology.
- It will help to study artifacts, provenance, and technology of past cultures more scientifically.
- The research will help archaeologists to know about the contribution of chemistry in archaeology.

Review of Literature

A lot of literature as a secondary source is available related to the research.

Archaeological Chemistry is written by A. M. Polard and Carl Heron deals with the new perspectives of archaeological chemistry. This is an introductory book (Polard and Heron 2008).

Archaeological Chemistry is written by Zvi Goffer describes new developments in analytical chemistry and in related disciplines, which have contributed to archaeological research (Goffer 2007).

Modern Analytical Chemistry is written by David Harvey is about the modern analytical techniques of chemistry (Harvey 2000).

Archaeological Chemistry: Analytical Techniques and Archaeological Interpretation is written by Michael D. Glascock, Robert J. Speakman and Rachel S. Popelka-Filcoff. The book deals with the analytical techniques to acquire more archaeological data (Glascock et al. 2007).

Scientific Methods and Cultural Heritage: an Introduction to the Application of Materials Science to Archaeometry and Conservation Science is written by Gilberto Artioli. It is about the application of archaeometry in conservation science of cultural heritage (Aritioli 2010).

Archaeology: A Very Short Introduction is written by Paul Bahnis a short introductory book of archaeological basic concepts (Bahn 1996).

Archaeological Field Methods: an Introduction is written by William S. Dancey. It is about some basic field methods in archaeology (Dancey 1981).

Field Archaeology: an Introduction is written by Peter L. Drewett. It is about different types of field methods used in archaeology (Drewett 1999).

Archaeology: the Basics is written by Clive Gamble. In this book the writer has described basic concepts of archaeology (Gamble 2001).

An Introduction to Archaeological Chemistry is written by Theron Douglas Price and James H. Burton is comprehensive text enhanced by color images, case studies, materials and research methods (Price and Burton 2012).

Analytical Chemistry in Archaeology is written by Mark Pollard, Catherine Batt, Ben Stern and Suzanne M. M. Young, is an introductory manual that explains the basic concepts of chemistry behind scientific analytical techniques and that reviews their applications to archaeology (Pollard et al. 2007).

Advanced Chemistry through Diagrams is written by Michael Lewis. This manual explains the advance concepts of chemistry. These concepts then can be applied to archaeology (Lewis 2001).

Math for Advanced Chemistry is written by Mike Robinson and Mike Taylor, this manual fully covers the new math requirements of the specifications. This combination can be applied to solve analytical problems in archaeology (Robinson and Taylor 2002).

Biochemistry is written by Monique Laberge deals with the study of chemical compositions of living organism and the chemical reactions that occur in them. It will help to understand chemical composition of past organisms (Laberge 2008).

Organic chemistry of Museum Objects is written by John Mills and Raymond White is a manual for the conservation of museum objects (Mills and White 2012).

Conservation Chemistry is written by Ted Listerand Janet Renshaw deals with the conservation of plastics, stone and wood (Lister and Renshaw 2004).

General Chemistry is written by Darrell D. Ebbing and Steven D. Gammon deals with online homework system, clear explanations of chemical concepts and problem solving approach. These concepts can be applied to revolutionize archaeology. (Ebbing and Gammon, 2009)

Introduction to Soil Chemistry Analysis and Instrumentation is written by Alfred R. Conklin is about analytical chemistry and its applications to soil. It will help to study archaeological soil (Conklin 2005).

Principles of Soil Chemistry is written by Kim. H. Tan deals with the new information of soil chemistry. This information will help to study archaeological soil (Tan 2011).

The Good Earth: Introduction to Earth Science is written by David McConnell, David Steer, Catharine Knight, Katharine Owens and Lisa Park. This book deals with the fundamental concepts of earth science. A relationship between earth science and archaeology can be made to apply chemistry on this combination (McConnell et al. 2008).

Archaeological Laboratory Methods: an Introduction is written by Mark Q. Sutton and Brook S. Arkush is about the basic methods to analyze archaeological materials. Methods relevant to chemistry can be concerned from this book (Sutton and Arkush 1996).

Lectures in Isotope Geology is written by E. Jager and J. C. Hunziker deals with the techniques to determine age by interpreting and analyzing isotopic data. These methods are very important for archaeology (Jager and Hunziker 1979).

Fundamentals of Analytical Chemistry is written by Douglas A. Skoog, Donald M. West, F. James Holler and Stanley R. Crouch. This is an introductory textbook of analytical chemistry that includes applications of Microsoft Exel in analytical chemistry (Skoog et al. 2011).

Advanced Chemistry written by Michael Culugston and Rosalind Flemming deals with advance methods of chemistry (Culugston and Flemming 2000).

Future Directions in Archaeometry: a Round Table is written by S. Taqueline Olin, deals with the future directions of archaeometry (Olin 1982).

Environmental Chemistry is written by Balarm Pani, deals with the application of chemistry in environmental science. It will help to study ancient environmental factors (Pani 2007).

Methodology

The research is cross-disciplinary with comparative analysis of chemistry and archaeology. Secondary sources have been acquired in the form of online databases, articles, conference papers, magazines and relevant books. The researcher has applied analytical chemistry and used Quantitative Analytical Methods for experiments as a primary source. The researcher has used XRD (X-Ray Diffraction), SEM (Scanning Electron Microscopy) and X-Radiography for the analysis of archaeological samples. The researcher has used the following scheme for Quantitative Analytical Method.

- **Choosing a Method**

The choice of a method for the analysis of a complex substance requires good judgement based on sound knowledge of the advantages and limitations of the various analytical tools available (Skoog 2011:1026).The researcher has used XRD, SEM and X-Radiography for the analysis of archaeological samples.

- **Acquiring the Sample**

The next step in quantitative analysis is to acquire the sample. To produce meaningful information, an analysis must be performed on a sample that has the same composition as the bulk of material from which it was taken (Skoog 2011: 7). The researcher has acquired seven samples in which five are pottery samples, one is unknown archaeological sample and the remaining one is an iron nail. All these samples were provided by my supervisor, Dr. Ghani-ur-Rahman.

- **Processing the sample**

Pottery samples were crushed and grinded in order to create homogeneity and to analyse them with XRD. The unknown archaeological sample was crushed into small pieces to make it ready for SEM. The iron nail was cleaned from dust to make its X-Radiograph. After processing these samples were labelled and placed in sample bags.

- **Eliminating the Interferences**

Once we have converted the sample into an appropriate form for measurement; the next step is to eliminate substances from the sample that may interfere with measurement (Skoog 2011:9). The researcher has eliminated all impurities from the samples.

- **Calculating and Measuring Concentration**

All samples are solid in nature.

- **Calculating Results**

Results of XRD and SEM are computerized and the result of X-Radiography is in the form of an X-Radiograph.

- **Evaluating Results by Estimating Their Reliability**

The researcher has estimated the reliability of results in order to get reliable analytical results.

Organization of the Research

The research is divided into following four chapters

- CHAPTER 1: Application of Chemistry in Archaeology
- CHAPTER 2: Scanning Electron Microscopy (SEM) of the Archaeological Material of District Shangla, Pakistan
- CHAPTER 3: X-Ray Diffraction (XRD) of the Pottery of Shere Pate, Kafiro Dherai, and Sar Pati, District Shangla
- CHAPTER 4: X-Radiography of Archaeological Metal Object of Buwagai, Chawgah, District Shangla

The first chapter is concerned with the methods and applications of chemistry that can be applied in archaeology. The second chapter is about Scanning Electron Microscopy and its application in interpreting the unknown archaeological material that is acquired from the District Shangla, Pakistan. The third chapter deals with the application of X-Ray Diffraction in the analysis of the pottery that is collected from the District Shangla. The fourth chapter is concerned with X-Radiography and its application to study an archaeological metal object of the District Shangla.

CHAPTER 1

Chemistry in Archaeology

What is Archaeology?

Archaeology is basically about three things: objects, landscapes and what we make of them. It is quite simply the study of the past through material remains (Gamble 2001: 15). The word comes from the Greek (arkhaiologia, 'discourse about ancient things'), but today it has come to mean the study of the human past through the material traces of it that have survived (Bahn 1996: 2).

Most archaeologists define archaeology as a sub-discipline of anthropology involving the study of the past through material remains. Archaeological methodology, theory and aims are different from anthropology and history but it solves the problems of these disciplines by providing data (Drewett 1999: 1). Archaeology has its own methodology, theory and aims by dealing with the remains of past peoples, societies and cultures (Drewett 1999: 2).

Most human beings have some interest in the past. Humans have always been curious about the traces left by their predecessors. A fifth-century Thracian princess in the Balkans had a collection of Stone Age axes in her grave. In North America; Iroquoian sites of the fifteenth and sixteenth centuries AD contain artifacts made thousands of years earlier; while in South America Inca emperors are said to have collected pottery of the Moche Culture. The earliest known 'archaeologist' was Nabonidus, king of Babylon, who, in the sixth century BC, excavated a temple floor down to a foundation stone laid thousands of years before (Bahn 1996: 8). In Greece during the first centuries AD the term denoted a category of actors who recreated ancient legends on stage through dramatic mimes! The term archaeology, as understood today, was reinvented by a seventeenth-century doctor and antiquary of Lyons called Jacques Spon. He also proposed the word 'archaeography', but that one fell on stony ground. In the Roman period, Julius Caesar's soldiers discovered many tombs of great antiquity when they were founding colonies in Italy and Greece; they rifled them for pots and bronzes, which were sold for high prices in Rome, an early example of grave-robbing and a trade in antiquities. Even the emperor Augustus was said by the historian Suetonius to have collected 'the huge skeletons of extinct sea and land monsters popularly known as "giant bones"; and the weapons of ancient heroes'. By medieval times, people in Europe were becoming intrigued by 'magic crocks', pots which mysteriously emerged from the ground through erosion or the actions of burrowing animals. At the same time, human-worked flints and polished stone axes were constantly turning up as farmers ploughed their fields. According to popular belief, these artefacts were elf-shot or thunderbolts, and in fact they were venerated and collected by peoples as far afield as Africa and India, often being used as amulets or charms. In Europe, many found their way into the 'Cabinets of Curiosities', collections of natural and artificial objects put together by early antiquaries, and realization slowly dawned in more minds that these 'thunderbolts' and 'magic crocks' were in fact the humanly made relics of ancient peoples. At the same time, discoveries of Greek and Roman sculpture were inspiring contemporary artists to study Classical forms, while wealthy families began to collect and display Classical antiquities (Bahn 1996: 9). It was in the sixteenth century that, in north-west Europe, some scholars really began to question Francis Bacon's claim that 'the most ancient times are buried in silence and oblivion', and recognized that information about the ancient past could be derived from the study of field monuments; a whole series of antiquaries in Britain, Scandinavia, and elsewhere started to visit and describe monuments. The seventeenth and eighteenth centuries saw these activities grow into a more systematic interest, accomplished by increasing numbers of excavations. While most digs were intended merely to retrieve objects from the ground, a few pioneers treated the work like a careful dissection, noting the relationships of artefacts to different layers of soil, and realizing that, on the whole, objects from upper layers must be younger than those from layers below. This new approach to interrogating and reading the ground and landscape like a document led to craze for barrow-digging. It makes a contribution to 'amateur' archaeology (Bahn 1996: 10). It was really only in the early to mid-nineteenth century that archaeology took over from antiquarianism, in the sense of aspiring to be systematic and scientific about the vestiges of the past. This was the period when, through discoveries in Western Europe of stone tools in association with now extinct animals, the great antiquity of humankind was first established and eventually became generally accepted. By the end of the nineteenth century, true archaeology was already a flourishing enterprise, with many of the 'great' hard at work-Petrie in Egypt, Koldewey at Babylon, Schliemann in the Aegean, and Pitt-Rivers in Britain. For most of these pioneers it was no longer a treasure-hunt but a search for information, and a means of answering specific questions. Through the twentieth century, thanks to the efforts of a whole series of major figures such as Wheeler in Britain and India, Reisner and Woolley in the Near East, Uhle and Kidder in America, Bordes and Leroi-Gourhan in France, it has become a massive, multi-disciplinary undertaking, drawing on the expertise of innumerable fields-from geophysicists and aerial photographers, to zoologists, botanists, chemists, geneticists, and a whole gamut of scientists who can produce dates from archaeological material or from the sediments that enclose it (Bahn 1996: 12).

Archaeology is a field of study that seeks answers to questions about the nature of human culture and society as it existed in particular times in the past, and about cultural and social change. From the earliest presence of human life on earth, the products and by-products of human activity have accumulated on and in the ground. These traces provide a link to past life ways and can reflect changes in behavioral patterns. Archaeology is the body of theory, method, and technique that guides the systematic recovery and analysis of the traces of past human activity. It enables scholars to bridge the gap between present and past cultures (Dancy 1981: 1).

Archaeology as a Scientific Discipline

Archaeology as a scientific discipline came into existence in the last part of the 20th century that is broadly defined as the application of scientific principles and methods to the characterization of materials that are related to cultural heritage. The field is so vast that there is no general agreement on the extent or even the definition of this discipline. The widely used term for the discipline is archaeometry, which has been in use since the founding of the journal *Archaeometry,* in Oxford in 1958. Before that Christopher Hawkes suggested using "archaeological science" to describe the discipline concerning the quantitative characterization of ancient objects and processes. Archaeometry is nowadays largely used as an alternative term for "archaeological science", or "science in archaeology". The application of scientific methods to archaeology requires a remarkable degree of interaction between specialists dealing directly with the different aspects of cultural heritage materials, such as archaeologists, curators, conservation scientists, art historians, and artists on one side, and scientists of different disciplines on the other. Most professionals involved with cultural heritage have a purely humanistic or artistic background but often they have no knowledge of scientific principles and techniques. The traditional academic separation between humanistic and scientific curricula in higher education has hindered the broad exchange of competences between art and archaeology, and science. The interface between disciplines is a fertile field where methodologies, analytical techniques, and especially the ideas developed in each specific scientific area may be enhanced, optimized, and ultimately applied with some ingenuity to diverse interdisciplinary environments (Artioli 2010: 1-3).

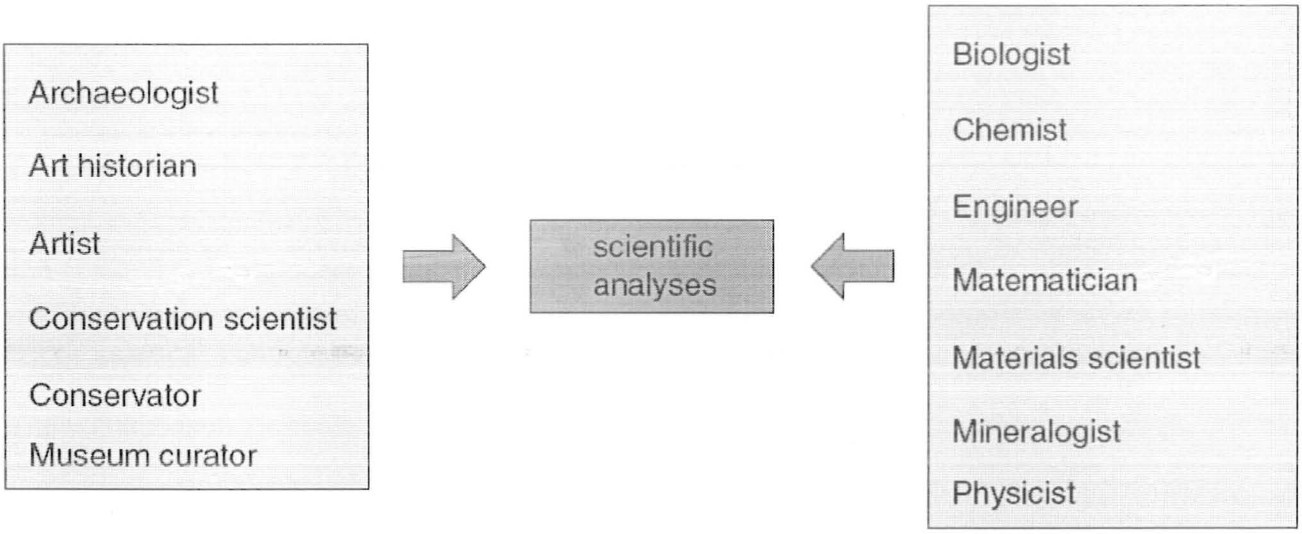

Figure 2: Science for the cultural heritage at the crossroad of a number of different professions and disciplines (Artioli 2010: 3)

What is Chemistry?

Chemistry is the science which deals with the composition and properties of matter and the laws or the principles which governs these changes. The discipline of chemistry is divided into different sub-disciplines, so that after getting basic knowledge of chemistry one can specialize in any discipline. Physical chemistry deals with the physical properties and physical behaviour of material things. Inorganic chemistry deals with all elements and compounds except the compounds of carbon. Organic chemistry deals with the compounds of carbon. Analytical chemistry deals with the analytical methods for getting information about chemical compounds and chemical processes. Biochemistry is the study of chemical compounds and their reactions occurring in living things (Clugston and Flemming 2000: 12).

Chemistry and Archaeology: a Mutual Relationship

Archaeology is the study of the human past through the material remains. There are many principles and methods in archaeology. Archaeological science is a kind of archaeology. Archaeological science includes laboratory methods used for the analysis of archaeological materials. Archaeometry is a branch of archaeological science that deals with the study of the chemical or physical properties of archaeological materials. Archaeometry helps to investigate the technology, chemical composition, chronology and other aspects related to archaeological question. Archaeometry is also called instrumental archaeology because it also deals with dating methods, geophysical instruments and study of DNA. Molecular archaeology is a term used for the study of organic molecules of archaeological chemistry to deal with ancient DNA in organic remains. Archaeology is therefore an interdisciplinary science. Interdisciplinary approach of chemistry and archaeology is called "archaeological chemistry" and it is a subfield of archaeometry. Archaeological chemistry deals with the knowledge of organic or inorganic composition, isotopes, molecules, elements and compounds of archaeological materials. Archaeological chemistry deals with the: Measurements of the chemical composition of various archaeological materials and determination of the original material of an unidentified thing. Identity and chemical composition are helpful in authentication, conservation and solving archaeological problems. Such research includes elemental and isotopic analysis of archaeological materials. As a result of such research one can come to know about status, demography, trade, residence, diet and subsistence of ancient cultures and their behaviour. By knowing the chemical composition of an archaeological object, it is then easy to conserve the object. The purpose of archaeological science is to learn about ancient cultures and to preserve their aspects for the future. Archaeological chemistry combines ideas, methods and principles of both chemistry and archaeology. It is at this interface of disciplines that extraordinary new research often takes place. Chemistry and archaeology are very different from each other. Therefore there are two groups of researchers. These two groups are archaeologists interested in chemistry and chemists interested in archaeology. There are a lot of archaeological questions that can only be answered through instrumental analysis but most archaeologists do not know about these methods. Similarly chemists know about such methods but have no knowledge of archaeology. Archaeologists rarely make collaborations with chemists or other physical scientists. These collaborations are very short-lived. Archaeological chemistry is a speedily rising field. For this reason, it is very vital that archaeologists are educated in chemistry and other physical sciences and more archaeological laboratories are constructed (Price and Burton 2011: 2-4).

Archaeological chemistry is an interdisciplinary field of archaeological research in which techniques and approaches from the chemical, biological, physical, geological, and statistical sciences are employed to extract more information from the material record of past human activity. The range of research conducted is so broad that any attempt to describe the field in a comprehensive summary is difficult. Major developments within archaeological chemistry have relied on the development and improvement of new techniques and procedures in conjunction with their application to significant archaeological problems (Glascock et al. 2007: xi).

A Brief History of Archaeological Chemistry

In order to know archaeological chemistry in a better way, a brief history of the field is important. The early history of chemistry is difficult to outline. Before written history, only a few basic elements that occur in nature were known. Elements such as copper (Cu), gold (Au), silver (Ag), lead (Pb), and tin (Sn) were known. Some of these elements began to be mixed, or alloyed, at the beginning of the Bronze Age around 5,000 years ago. Their chemical properties were known. Copper and tin were mixed to make bronze. In the middle of the seventeenth century the first element, phosphorous (P), was discovered through scientific inquiry. By 1860, 63 elements had been described. At the beginning of the nineteenth century, most people did not know that the earth and their ancestors had a deep past in time. It was the middle of the nineteenth century, when natural scientists discovered the relationship of human artifacts with the bones of extinct animals. Archaeology became an academic discipline only toward the end of the nineteenth century. Archaeology is less than 150 years old. A combination of chemistry and archaeology, archaeological chemistry also has an important history. Early investigations in archaeological chemistry were carried out by chemists. Initial studies focused on one or a few elements to resolve problems about chronology and the authentication of artifacts. It also focused on questionable antiquity, and site discovery. In the mid-nineteenth century, an Austrian chemist discovered that the chemical composition of archaeological materials could be used to identify their origins. In the 1860s a French geologist argued that the sources for Neolithic stone axes could be determined by their composition. Otto Helm, a Polish pharmacist, began the study of the composition of amber beads from excavations at the Greek site of Mycenae in the 1890s. it was to determine their place of origin. One of the first studies of the chemistry of prehistoric pottery was published in the Journal of the American Chemical Society in 1895.The first half of the twentieth century delivered a series of new studies. These were technologies that resulted from the military research motivated by world wars. The introduction of instrumental methods such as optical emission spectroscopy (OES) initiated several major research programs concerned with the origins of bronze in Europe. Thousands of bronze objects in Europe were analysed in these studies. In the 1930s, the Swede Arrhenius published a series of articles about the use of phosphate analysis to identify archaeological sites. Phosphate accumulates in places of human habitation because of accumulations of bone, feces, and other organic materials in the soil. Arrhenius used this knowledge and a rapid analysis technique to take samples of soils over a large area and conclude their phosphate concentrations. High levels of phosphate usually discovered the location of an ancient settlement. His work was followed by the use of other elements as indicators of past human activity. Lutz (1951) observed concentrations of phosphorus, nitrogen, potassium, and calcium in soils from archaeological sites in Alaska. Cook and Heizer (1965) investigated calcium, nitrogen, and phosphorus as important indicators of past activity at California sites. Another early example of archaeological chemistry involved the Piltdown discovery in England from the first part of the twentieth century. A human skull and ape jaw were joined together and marked to appear ancient. The falsification was passed to experts as the "missing link" between apes and humans. It took almost 40 years for new techniques to expose the cheating. Kenneth Oakley and his colleagues at the British Museum of Natural History reanalysed the Piltdown materials in the late1940s. They used a new "Fluorine Absorption" test and measured concentrations of fluorine as well as iron, nitrogen, collagen, organic carbon, organic water, radioactivity, and crystal structure in the bones. Fluorine absorption can provide a kind of relative age for bone samples. Teeth and bones absorb fluorine from groundwater environment. The fluorine reacts with phosphate hydroxyapatite (the mineral component of teeth and bones) to form fluorapatite. This reaction is assumed to be relatively constant in nature. Thus, the amount of fluorine present in the fossils from the same locality should be the same if they were deposited at the same time (Price and Burton 2011: 15-16).

Oakley's work showed different levels of fluorine between the skull and the jaw of Piltdown man. The results were published in 1953 and Piltdown was finally removed from the list of our ancestors. About the same time archaeological dating came with the discovery of radiocarbon. Willard Libby recognized the nature of radioactive carbon and the significance of its short half-life. Carbon occurs in all living things. When those things die, the radiocarbon in their bodies begins to decay. After some 5,730 years, half of the 14C has disappeared and that dissolution continues until the radioisotope is gone. That process allows archaeologists to determine the age in calendar years of wood and charcoal, bone and fiber, seed and from the present until almost 40,000 years ago. Libby received the Nobel Prize for his discovery of radiocarbon in 1960. Much significant work in archaeological chemistry has been done in the last50 years. A multitude of new ideas, instruments, and procedures have been added to the archaeological chemistry. The evolution of both methodology and instrumentation in quantitative chemistry has allowed more detailed descriptions of the composition of a variety of archaeological materials. Today, a number of approaches and techniques provide new information about the past. The first specialized journal in the field, Archaeometry, appeared in 1958, followed by the Journal of Archaeological Science in 1974 (Price and Burton 2011: 17-18).

All the research on atomic reactions led to the development of the technique of Neutron Activation Analysis (NAA) after the Second World War. NAA and other methods were used forth chemical characterization of copper, tin, obsidian, and other raw materials. Some of the most impressive examples of archaeological chemistry in action in recent years have come from the study of unusual human remains. Ötzi the Iceman from the Italian Alps and Kennewick Man from the State of Washington are two cases. The Iceman is the name given to the remains of a body frozen for 5,000 years in a glacier in the Italian Alps. Since that time almost every known kind of archaeological science has been applied to his remains to learn about the man and his activities before he died. A similar situation has arisen with the human skeleton found along the

Kennewick River in Washington in 1996. The discovery is very important because its radiocarbon age of 9,300 years before the present makes the skeleton one of the oldest in the North or South America. The skeleton is also important because it is the central point of a debate between archaeologists, who want to study these remains, and Native American groups in the state of Washington, who want to rebury this individual. Recently, the courts have ruled that the archaeologists could study the skeleton; the full range of archaeological science is now being applied to the bones and teeth of Kennewick Man. Today, the evolution of both method and instrumentation in quantitative chemistry is providing more detailed descriptions of the composition of a variety of archaeological materials. Elemental and isotopic analyses of archaeological objects tell about subsistence and diet, exchange and trade, habitation, demography, status, and other aspects of ancient cultures. Organic studies are concerned with the eating habits, raw materials, agricultural fields, dyes and oils, and much more about the past. (Price and Burton 2011: 18)

Laboratory for Archaeological Chemistry

Laboratories for archaeological chemistry are found in various parts of the world, usually associated with either universities or museums. Laboratories often have a focus on a particular kind of analysis. Some labs do isotopic research; other labs do elemental analyses or organic chemistry. Some places conduct a variety of different kinds of studies. In Pakistan there is no laboratory of archaeological chemistry to investigate stone, pottery, bone, soil and other elements and isotopes. Archaeological chemistry is done in laboratories that have the equipment, instruments, and facilities necessary for such research but unfortunately Pakistan has no such facilities. The instruments range from microwave- to room-size and require elaborate electrical, plumbing, gas, cooling, and ventilation installations. The instruments, their installation, support, and maintenance are not cheap and a developing country like Pakistan is unable to support such instrumentations. In addition to the instruments, laboratories require a complex of equipment for sample preparation, involving extraction, cleaning, washing, weighing, burning, powdering, and dissolving. This requires work places, very pure water, fume hoods, furnaces, drills, mills, balances, and much more. Samples to be powdered require drying ovens and grinding mills. Samples that must be dissolved require strong acids and heating equipment. Samples to be converted into a gas require vacuum lines and a series of pumps, filters, heaters, and frigid liquids to extract the sample for analysis.

Figure 3: Situation of the Conversation Lab of Taxila Museum, Pakistan

Following list is about the laboratories of archaeological chemistry in the world. Unfortunately there is no such laboratory in Pakistan to place it in the list.

Aghia Paraskevi Attiki, Greece	Laboratory of Archaeometry
Alexandria, Egypt	Laboratory of Archaeometry
Amsterdam, Netherlands	Institute for Geo- and Bioarcheology
Ankara, Turkey	Archaeometry Program, Middle East Technical University
Beijing, China	Department of Scientific History and Archaeometry
Bradford, England	Department of Archaeological Science
Cagliari, Italy	Dipartimento di Scienze Archeologie e Storio Artistische
Cambridge, England	MacDonald Institute for Archaeological Research
Cambridge, Mass	Center for Archaeological Materials
Columbia, Missouri	Archaeometry Laboratory
Knoxville, Tennessee	Center for Archaeometry and Geochronology

Leuven, Belgium	Centre for Archaeological Sciences
Liege, Belgium	Centre Européen d'archéometrie
Madison, Wisconsin	Laboratory for Archaeological Chemistry
Mannheim, Germany	Curt-Engelhorn-Centre for Archaeometry
Mexico City, Mexico	Archaeometry Laboratory
Oxford, England	Research Laboratory for Archaeology and the History of Art
Orlean, France	Institut de Recherché sur les Archéomatériux
Philadelphia, Pennsylvania	Museum Applied Science Center for Archaeology
Rehovot, Israel	Kimmel Center for Archaeological Science
Stockholm, Sweden	Archaeological Research Laboratory
Tampa, Florida	Archaeological Science Laboratory
Tempe, Arizona	Archaeological Chemistry Laboratory

Urbana, Illinois	Environmental Isotope Pale biogeochemistry Laboratory
Zaragoza, Spain	Research Laboratory for Cultural Heritage

Table No. 1. Selected List of Archaeological Chemistry Facilities in the World (Price and Burton 2011: 19)

Following equipment are required in the laboratory of archaeological chemistry. Such laboratories can be made with these equipment at Taxila Institute of Asian Civilizations, Quaid-i-Azam University, Islamabad Pakistan, with the collaboration of foreign laboratories.

Ratio mass spectrometer	ICP/AE spectrometer
Analytical mill	Chemical hood
Freeze dryer	Air compressor
Electronic pH meter	Desiccating cabinet
Ultrasonic water bath	Muffle furnace
Air abrasive cabinet	Hot plate

Ultrasonic cleaners	Ultrapure water still
Micro electro balance	Vacuum pump
Repipet dilutor	Electronic balance
Petrographic microscope	Drying oven

Table No. 2. Some equipment used in the Laboratory for Archaeological Chemistry (Price and Burton 2011: 20)

What Archaeologists Want To Know

There are a lot of questions in archaeology that archaeologists want to answer. How do we understand the lives of peoples in the past from the bits and pieces of tools and trash, the ruins and mounds that still survive? This is a big problem for archaeology. In order to help solve this problem, archaeologists use a structured way to investigate our ancestors and their ancient societies. This framework of enquiry involves archaeological cultures, time, and space (Price and Burton 2011: 25-26).

Archaeological Cultures

In the past world, archaeological cultures are identified by artefacts such as stone or metal tools, or pottery, or unique building styles, or a combination of such features. An archaeological culture shares space, time, and material culture. Thus, archaeologists identify archaeological cultures in the past and tend to equate them with distinct societies. In fact, one cannot identify specific societies in the past because of the fragmentary nature of the archaeological record that survives and the problems of defining the time and space boundaries of such groups (Price and Burton 2011: 26-27).

Time and Space

This aspect of archaeology is known as culture history, determining the chronology and distribution of past cultural groups. Time is a special component of an archaeologist's viewpoint. It is essential to know the age of the materials under study in order to be sure with change overtime. Archaeologists have spent a great deal of effort learning about the passage of time and finding ways to measure it. There are different ways of determining the antiquity of archaeological materials. Relative chronology can provide the near age of past things. More useful is absolute chronology that measures the age of materials in calendar years before the present. Absolute chronology is laboratory science that involves complicated instrumentation and chemistry. The most common methods for measuring time in calendar years use annual events recorded in nature (e.g., tree rings, annual layers in ice or sediment) or radioactive decay. Dendrochronology is a method for using tree rings to date wood found at archaeological sites. Radiocarbon dating employs the radioactive decay of carbon to determine the time of death of organic materials. Space refers to the geographical location and distribution of the archaeological materials of interest. Questions about past archaeological cultures focus on features of society such as technology, economy, social organization, ideology, and demography. These are the big questions about the past. With some understanding of these features, one can begin to understand these past societies. Information on technology and economy are generally more accessible in material culture, than social organization and ideology. All these aspects are of special interest in archaeological chemistry (Price and Burton 2011: 27-28).

Environment

Environmental researchers apply information and techniques from the earth and biological sciences to study relationships among peoples and their environments using organic and inorganic evidence from archaeological sites (Reitz et al. 2008: 3). Advances in instrumentation for the observation and measurement of biological, planetary, and astronomical environmental phenomena have driven unprecedented recent growth in the historical geosciences as well as biosciences (Jones 2011: 3). There are two important components of the environment in which societies exist. The physical environment (topography, climate, water, vegetation, soil, rocks, and minerals) provides the necessary resources and conditions for human society. The cultural environment refers to the humanly created environment, as well as relationships with other human groups in the physical environment. The physical environment in which people live affects their lives in many ways. The physical environments can provide or lack important mineral, water, or other resources. Archaeologists investigate the environmental context of ancient societies in detail. An important point to remember is that environments change over time. It is essential to determine the nature of the environment during the time of an archaeological culture. As an example, the Sahara Desert today is one of the drier areas on earth, but 8,000 years ago this area had rivers and extensive vegetation and supported numerous villages of herders and farmers. The cultural environment is a result of human activity. Archaeology seeks to define and understand both types of environments in discussions of past human behavior (Price and Burton 2011: 28-29).

Technology

Technology refers to the methods, materials, knowledge, and organization for making and using tools, equipment, facilities, and structures to control and adapt to the environment. The fragments of the tools and architecture that people used in the past, made of long-lasting materials such as stone, ceramic, and metal, are the most common archaeological remains. Technology is a very human means for survival and success. Humans lack sharp teeth or claws; technology provides cutting edges on stone tools. Humans do not have fur or heavy body hair against the cold; technology provides fire, clothing, and shelter. As technology becomes more complex and elaborate over time, more steps, more materials, more organization, and more knowledge are often required. What was a stone blade used for? Was this ancient pottery vessel used for cooking, storage, or another purpose? Was this fireplace for heat or cooking or firing pottery? Was this room used for residence or religious purposes? There are many such questions that arise in the finds from any excavation. These questions do not have easy answers, but archaeological chemistry can often help to provide some clues (Price and Burton 2011: 29-30).

Economy

Economy concerns the way in which people obtain, produce, and use the things they need to survive. Such things include food, shelter, raw material, and information. If technology refers to the methods, tools, and information for making equipment, facilities, and structures for survival and growth, economy is the way to obtain and produce these necessary things (Price and Burton 2011: 30).

Food

Food is the most clear need for human groups to survive. Subsistence is the term commonly used in archaeology for the foods and subsistence pattern is used for different ways of obtaining food. There are several major patterns of obtaining food observed during the course of human prehistory: gathering, scavenging, hunting, and farming. Earliest human beings were largely vegetarians, like the chimpanzees. These early ancestors collected and gathered leaves, seeds, roots, and other vegetable food as part of their daily fare. The importance of meat in early human diets is unclear. There is increasing evidence that chimps occasionally hunt and eat small animals. At the same time, the bones of large game are sometimes found at early archaeological sites. The origin of agriculture involves the domestication of plants and animals for human use and consumption. Farmers began, first about 10,000 years ago, to control the wild. The first farmers cultivated and herded on a limited scale. Fields of crops and herds of animals were small. Hunting and gathering continued to provide some of the food that these groups were eating. As human societies grew in size and complexity over time, however, farming became more intensive and technologies more complicated in order to increase crop yields. Irrigation, terracing, raised fields and other techniques were invented to enhance food production. Archaeologists who study animal bones and plant remains can provide essential evidence about past human diets and can often distinguish between hunting and gathering and farming. Archaeological chemists also play an important role in such investigations. Various kinds of isotopic and organic analyses can help with the determination of past subsistence patterns and the importance of different kinds of foods (Price and Burton 2011: 30-31).

Shelter

Shelter takes many forms from caves to fallen trees to built huts and houses and palaces. Archaeological science assists in the study of the places where people lived and the kinds of activities that took place there. Specifically the discovery and investigation of human settlements is an important component of archaeological chemistry. The search for ancient places involves many techniques including air photography, georadar, magnetometry, and many others. One method of searching involves the chemical composition of soil samples, focusing primarily on the element phosphorus. The analysis of the chemical composition of the floors of houses and other areas within human settlements also can tell us about the activities that were taking place (Price and Burton 2011: 31).

Raw Material and Production

All societies depend on raw materials for the food, shelter, tools, facilities, and structures and infrastructure. Most of these needed materials can usually be found in the local environment. Food, stone, clay, and wood are basic materials for many prehistoric cultures. On the other hand, many societies want or need raw materials that are not found locally and must be obtained by trade or conquest (Price and Burton 2011: 31-32).

Exchange

Exchange is an important aspect of economy. One way to study interaction within and between societies is to look at the distribution of items of exchange. Individuals and groups exchange materials and ideas. When artefacts such as stone axes, obsidian knives, metal spear points or certain kinds of food pass from person to person, or group-to-group, archaeologists speak of "exchange."Three kinds of exchange can be distinguished: reciprocity, redistribution, and trade.

Archaeologists usually focus on "exotic materials" in the study of exchange and trade. The presence of objects and materials that are not available or locally produced in an area provides immediate evidence of interaction and external connections (Price and Burton 2011: 32).

Organization

Archaeologists usually combine social and political organization to discuss the how past peoples related to one another, both those nearby and those distant. Social organization refers to the structure of relationships within a particular society, ordered by kinship, marriage, and status. Political organization refers to the use and distribution of status, power, and authority within a society. Settlement pattern is the term used to describe how human groups are organized geographically in region. Settlement patterns reflect the social and political organization of society as well as the use of the landscape (Price and Burton 2011: 34).

Ideology

Ideology refers to the set of doctrines, beliefs, and norms that guide the beliefs and practices of human societies. Ideology is society's model of how the world works. Ideology helps society to justify specific rules, practices, and behaviours. Ideology, often in the form of religion, helps to explain the unknown and provides answers to existential questions. Ideology is reflected in the clothes we wear, the food we eat, and the places in which we live. The term ritual is sometimes used to describe material remains that are not readily understood in terms of technology, organization, or economy. In the study of the past, however, it is difficult to distinguish the ideological from the realistic. Because the material correlates of ancient beliefs, cosmologies, and ideologies are usually unknown, it is difficult in archaeology to identify which objects and architecture are ideological and which serve more practical and immediate purposes (Price and Burton 2011: 38).

Archaeological Materials

The range of raw materials that humans use for food, construction, valuables, transportation, and other purposes is enormous. Many materials are found at archaeological sites. In order to understand chemically analyze the materials found at archaeological sites; it is essential to understand something about their context, sources, technology, use, and disposal. Common archaeological materials are rock, pottery, bone, sediments, metals, and other things like shell, pigments, charcoal, and plant remains (Price and Burton 2011: 41-42).

Rock

Rock is any consolidated, compact, hard or soft natural material consisting of one or more conglomerated minerals. The rocks that make up the crust of the earth consist of either single minerals or natural cohesive aggregations of grains of minerals held more or less firmly together into a solid mass. Many rocks are mixtures of two or more different minerals and are, therefore, heterogeneous materials, while some, composed of only one mineral, and therefore known as monomineral rocks, are homogeneous materials. Examples of the latter are marble, which consists entirely of calcite (composed of calcium carbonate), and alabaster, which consists of consolidated plaster of Paris (composed of calcium sulfate).Mineral or rock that has been naturally or artificially broken, cut, or otherwise shaped to serve some human purpose is known as stone. For millions of years, long before the discovery of the metals, humans used stone for making tools; erecting houses and monuments; building roads, floors, and roofs; sculpting statuary; and carving ornaments. It is not surprising, therefore, that stone is one of the most frequently encountered materials in archaeological excavations (Goffer 2007: 24-26).

The study of archaeological stone is based mainly on chemical, physical, geological, and mineralogical investigation; this entails identifying the composition of the stone, characterizing its structure and other physical properties. The main objective of analysing archaeological stone, as well as most other archaeological materials, is usually to identify the rock. This is not, however, the only objective, since the results of chemical analyses often also provide insights into any weathering processes that the stone may have undergone as well as its provenance and chronology (Goffer 2007: 26-27).

Stone artefacts date back earlier than two million years, and are often the only remaining evidence at early archaeological sites. Indeed, "Palaeolithic" – the Old Stone Age – is the name given to deepest antiquity. When the Mesolithic and Neolithic are included, the Stone Age comprises a period from roughly 2.6 million years ago to approximately 4,000–5,000 years ago, or 99.8% of history. During this time stone artefacts evolved from the earliest Oldowan scrapers, choppers, and hammerstones into a highly diverse array of tools and other items including the use of stone for ornaments, pigments, ritual objects, construction materials, grinding and polishing, projectile points, and many other purposes. Archaeologists commonly describe stone tools functionally in terms of their use (e.g., flake, projectile point, borer, lithic debitage, groundstone, etc.); archaeological chemists focus upon the compositional characterization of these materials. This begins with the geological identification of the stone, i.e., what type of rock, and might proceed to an analysis of the minerals composing the rock to further analysis of the major, minor, and trace elemental composition and event an isotopic characterization, depending upon the specific research questions. Functional characterization often takes place in the field, and an archaeologist familiar with the materials can usually further distinguish items geologically inters of different kinds of rocks, e.g., as greenstone, chert, obsidian, or marble. Rock types can be identified at a relatively basic level without extensive geological training by recognizing a few textural attributes such as grain size and alignment and the homogeneity or heterogeneity of the texture, along with an ability to recognize about a dozen common rock forming minerals. There are many thousands of minerals, less than a few dozen minerals include the major components of almost all rocks. Minerals have, by definition, not only a well specified chemical formula (e.g., $CaCO3$ for calcite and $SiO2$ for quartz), but also a specific structure. Two minerals can have an identical chemical composition, but different structures, and thus be quite distinct minerals, with different properties. Probably the most commonly given example of this is graphite and diamond. Graphite is pure carbon with the carbon atoms bound to each other in sheets but the sheets do not share electron bonds between them. The sheets can slide easily over one another, without breaking chemical bonds, causing graphite to be among the softest of all minerals. Diamond is also pure carbon but each carbon atom is bonded to four other carbons in a three-dimensional array and is the hardest known substance (Price and Burton 2011: 43-44).

Rock	Type	Appearance	Major minerals
Basalt	Igneous	Fine-grained, homogeneous Dark, Brown, blue-grey, black	Feldspar, pyroxene, olivine
Andesite	Igneous	Fine-grained, homogeneous. with inclusions, usually medium brown or blue-grey tones	Feldspar, amphibole

Rhyolite	Igneous	Fine-grained, homogeneous, with inclusions	Feldspar, mica, quartz
Obsidian	Igneous	Fine-grained, homogeneous, green to gray to black	Quartz
Gabbro	Igneous	Dark, Coarse-grained, not banded	Feldspar, pyroxene, olivine
Diorite	Igneous	Coarse-grained, light and dark minerals, not banded	Feldspar, amphibole
Granite	Igneous	Light or pink, Coarse-grained, heterogeneous	Feldspar, mica, quartz
Shale	Sedimentary	Usually dark, Soft, Fine-grained, homogeneous	Clay
Sandstone	Sedimentary	Sand-sized grained	Quartz, feldspar
Limestone	Sedimentary	Usually fine-grained, light-colored, soft	Calcite
Slate & phyllite	Metamorphic	Usually dark, fine-grained homogeneous and may be shiny (from shale)	Clay, mica
Quartzite	Metamorphic	Hard, glassy, sand-sized grains(from sandstone)	Quartz
Marble	Metamorphic	Usually light-colored or white, softer than steel (from limestone)	Calcite
Gneiss	Metamorphic	Coarse-grained, homogeneous (from granite and others)	Feldspar, amphibole, mica, quartz

Table No. 3. Types of rock and their important characteristics (Price and Burton 2011: 45)

Calcite and aragonite is another similar mineral pair. They are both calcium carbonate, CaCO3, but have different structures. Shell, for example, commonly contains layers of both these minerals, which can be distinguished in the microscope by their optical properties. Thus, while chemical methods can be often be used to suggest a particular mineral, the definitive identification requires recognition either of distinct physical properties most commonly by observation of unique optical properties in the petrographic microscope or by direct determination of its crystal structure through X-ray diffraction (XRD). One should recognize this distinction between X-ray diffraction, which reveals structure but does not provide direct compositional data, and X-ray fluorescence (XRF), which is a spectral technique that gives composition, and not structure. Knowing the type of rock also places strong constraints upon the geographic source of the material. There are also a large number of geological materials such as native metals, precious stones and gems, and pigments that are not among the common rocks and minerals but the importance of which significantly outweighs their shortage in the archaeological record. Because such materials are scarce, with lightly distributed sources, and highly valued, their presence in an archaeological context can imply development of distant resources and possibly imply exchange or other interaction with distant societies. Other geological materials that have received considerable interest from both archaeologists and archaeometrists include jade, turquoise, marble, metal ores, native metals, and chert. Analyses of such geological materials sometime require basic identification studies of fine grained pigments and stones that cannot be identified by eye or microscopically. For the identification of such fine-grained materials, X-ray diffraction (XRD) and Raman infrared spectroscopy are commonly employed. XRD is more commonly applied to powders, but cane difficult to interpret on complex assemblages of more than a few minerals. Raman IR has an advantage in the case of solid stones of being non-destructive. Other studies on stones beyond identification and provenience studies include microscopic studies of use wear and analysis of possible residues for DNA or other, biologically distinctive organic molecules (Price and Burton 2011: 46-47).

Pottery

Clay is the generic name for very fine grained, unconsolidated earthy minerals that are supple and pliable when wet, become hard and retain their shape when dried, and turn into a stony material, known as fired clay , when heated to red heat. It is because of these unique properties that very early in the development of humans, clay became a most important raw material, used to make bricks, pottery, and later, other ceramic materials. Clay absorbs and loses water easily, and the water absorbed penetrates the surface of the grains, which swell accordingly and shrink when they lose the water. The grains also adsorb gases: their surface takes up and retains gases such as carbon dioxide and water vapour (in the soil, the gases adsorbed on clay particles are used as nutrients by plants) (Goffer 2007: 231).

Chemically, all clays are composed of oxides of silicon, aluminium, and hydrogen, namely, silicon dioxide, aluminium trioxide, and water in a weight proportion that can be expressed by the general formula $\mathrm{Al2O3 \cdot SiO2 \cdot 2H2O}$ (Goffer 2007: 232).

While stone tools have been used for millions of years, fired clay figurines do not appear in the archaeological record until approximately 25,000 years ago and useful pottery first is made only about 16,000 years ago. Made from relatively unpreserved clay, but strengthened by firing at high temperature (>700 °F), ceramic materials are much harder and more durable than the original raw clay. Potsherds, broken fragments of ancient ceramic vessels, persist in the archaeological record; even for sites several millennia old ceramic fragments often include the major portion of the present material record. Because ceramic raw materials are plastic and may be shaped into virtually any form imaginable, their morphological and functional diversity is enormous, making them among the most studied of all archaeological materials. The most basic level of analysis, identification of ceramic material, is readily made in the field. The next level of analysis, the raw materials that were used, is usually done to determine the geographic source of the pottery. This usually includes morphological and stylistic information that assigns the ceramic to a culture area and time period, but might also involve compositional analysis, either mineralogical or elemental to determine more specifically where the pottery was made. Although all ceramic materials are necessarily made from clays, firing alters the structure of clay minerals such that their original mineral structure is destroyed and difficult or impossible to determine, either microscopically or by X-ray diffraction. Chemical analyses are frequently attempted to determine the geographic origins of pots, possibly being among the most common of all archaeometric studies. A comparison of the compositions of locally obtained potsherds, both with and without the exotic style, to the compositions of sherds from the distant region can provide evidence to directly resolve such a question. If they differ from the distant pots but resemble the local ones suggests local emulation; if they resemble the distant pots and differ from the local ones, then importation is implied. If they resemble neither set, then new hypothesis, and possible line of inquiry, is needed (Price and Burton 2011: 46-49).

Bone

Zooarchaeology refers to the study of animal remains excavated from archaeological sites (Reitz and Wing 2008: 1). Bones or objects made of bone material are an important part of the archaeological remains and can largely contribute to the understanding of ancient societies as they give evidence of human or fauna occupation, climatic and environmental conditions (Alain

2006: 255). Bone is found on archaeological sites when conditions of preservation allow. Bone most often occurs at the inedible waste of meals or the remains of human burial. In addition, bone and other skeletal tissue from animals (teeth, antler, shell, and horn) were often used to make certain kinds of tools and equipment. Archaeozoologists are trained to identify the genus and species of animal from small pieces of bone, as well as to determine the age and sex of the animals, how bone was fragmented, and how many individual animals are represented in a setoff bones. Bone can answer questions about whether animals were scavenged, hunted, or herded, their age and sex, about how animals were butchered, about how important meat was to the diet, when animals died, and the process of domestication. Similar kinds of information are present in human remains. The human skeleton is much more than a structural framework for supporting our bodies. Tooth enamel is the hardest part of our skeleton and is composed largely of the mineral apatite with virtually no organic component. Tooth enamel often preserves even under harsh burial conditions. Bone, a combination of mineral and organic matter, is more susceptible to decomposition and contamination. The distinction between cortical and trabecular bone tissue is an important one in understanding the survival of skeletal parts. Most bones contain both kinds of tissue. The proportion of cortical and trabecular bone varies in the different bones of the skeleton. Cortical bone is the hard, dense bone that provides support and strength in the skeleton, and is more common in the limbs. Trabecular bone is the spongy bone tissue that makes up the interior of ribs, vertebrae, the pelvis, and other bones. Trabecular bone provides less structural support in the skeleton, but has an important role in metabolism. Because of the more porous and softer nature of trabecular tissue, it is usually the first type of bone to decompose during burial. An enormous amount of information about both deceased individual is stored inhuman bones. Information on age and sex is recorded in the skeleton. The length and thickness of long bones provide an indication of an individual's size and strength. Evidence of disease or illness is often embedded in bone. It is often possible to determine age at death, cause of death, sex, history of disease or accident, occupation, movement, and nutritional status from the analysis of prehistoric human bone. Because bone is organic, it sometimes holds ancient DNA that can tell us many things about past activities and genealogical relationships. Bone itself is a dynamic, cellular tissue with both structural and physiological functions. Bone makes up the skeletal frame that supports our body and provides the connections for movement. Bone also plays an important role in the metabolic and haematological functions e.g., bone marrow produces white blood cells. These activities and functions require a complex substance. Bone is in fact a remarkable "space-age" material, a composite of organic molecules and mineral crystals. Bone tissue is essentially a network of mineralized fibers, composed of a matrix of organic collagen filled with inorganic calciumphosphate (apatite) crystals. Bone has three major components: a mineral fraction (apatite), an organic matrix (collagen), and water. By dry weight, the organic materials constitute about 30% and minerals about 70% of bone. Bones and teeth are created by adding mineral crystals to collagen. In addition to the major components calcium, phosphate, and water, a number of minor and trace elements are incorporated during the manufacture of bone tissue. Hydroxyapatite (Ca, Sr, Ba) 5(PO4)3(OH, F) is the major mineral component of bone and enamel and provides the hardness to these tissues. Collagen is a major structural protein, forming molecular cables that strengthen the tendons and vast, resilient sheets that support the skin and internal organs. Collagen contains one quarter of the all of the protein in your body. Collagen comprises 90% of the organic portion of dry, fat free bone. In spite of its essential nature, collagen is a relatively simple protein. Its major components include acetic acid, proline, and 4-hydroxylproline (e.g., 21(C5H9NO3).Bone tissue is created from the minerals and organic molecules that entered the body through drinking water and food and the chemistry of human bone holds information on the diet and life history of the deceased individual. Both the elemental and the isotopic composition of bone are important in studies concerned with dietary reconstruction. Elemental analyses focus on the mineral portion of bone, while isotopic studies are usually aimed at the organic part. Isotopic analyses are also used to study place of origin and past climate as recorded in tooth and bone (Price and Burton 2011: 49-51).

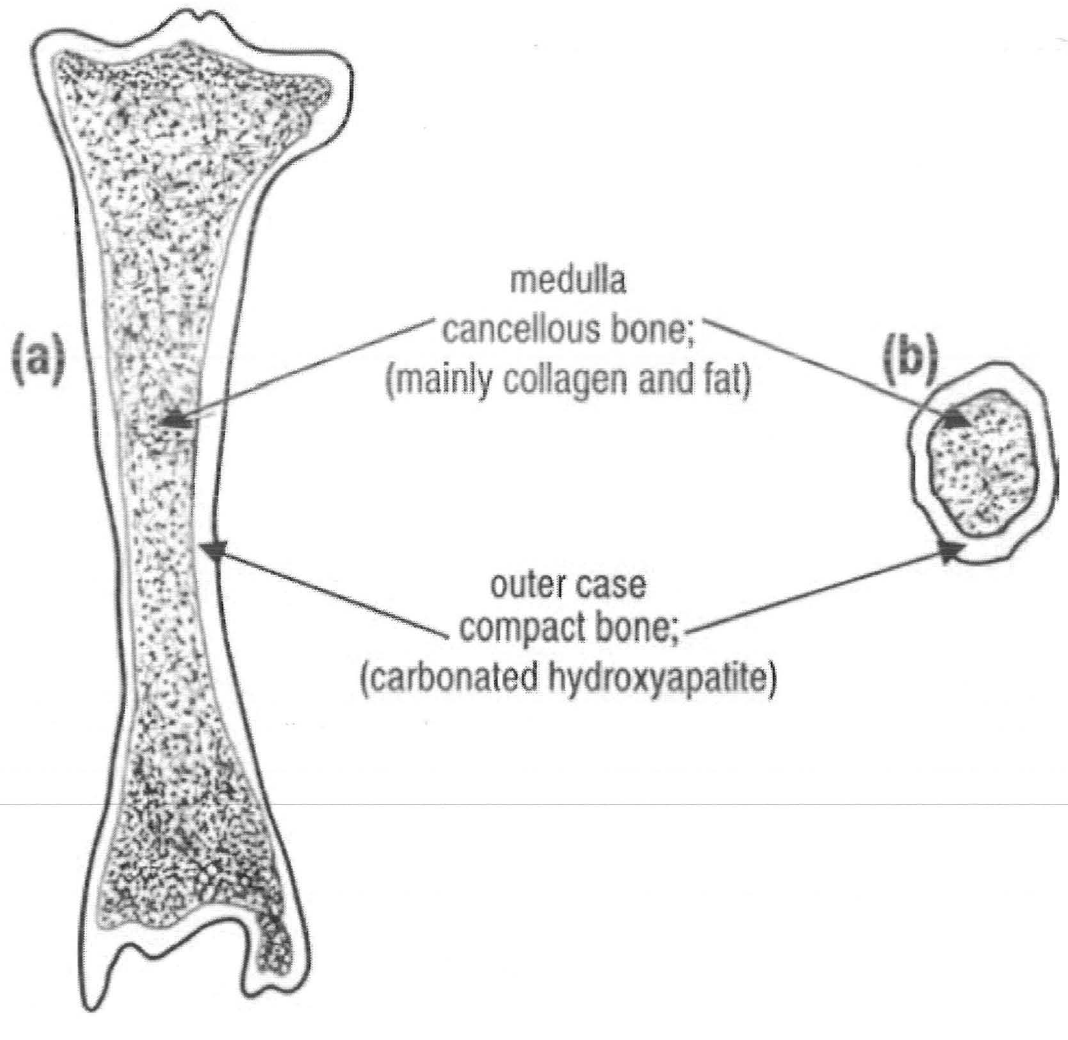

Figure 4: Bone; longitudinal and Transversal Cross Sections (a) an transversal (b) cross sections of a long bone (Goffer 2007: 381).

Sediment and Soil

Sediment is an important term in geoarchaeology. Sediment is any particulate matter (clay, sand, silt, gravel, leaves, shell, and other materials) that can be transported by water or other fluids. Sediments are eventually deposited as a layer of solid particles. Sediments make up the earth's entire surface that is not water or rock. Virtually all buried archaeological materials are found in sedimentary deposits. Rocks take a long time to form and most archaeological materials are simply too young to end up in a layer of rock. Soil is a special kind of sedimentary deposit produced in situ by the weathering of the earth's surface. Weathering refers to the chemical and biological processes that operate to breakdown and change the surface of the earth, altering its colour, texture, or composition. These processes include rainfall, frost, and plant and animal activity as major forces of change. Soils are not only found on the surface of the ground. Old soils can be buried by later deposits. Buried soils provide a useful marker of the location of former land surfaces. Soils form on the surface of sediments and usually exhibit zones of weathering that reflect changes in the physical and chemical nature of the deposit. There are many different kinds of soils depending on the type of parent material and the conditions of weathering. Soils also vary with temperature, rainfall, and the type of vegetation present. Most soils, however, share common features related to the process of weathering and the solubility of the material. Most soils exhibit several strata or horizons that form during their development. The top of the soil is the organic or O horizon and contains dust, leaf litter, and other organic materials that accumulate on the surface. This horizon is normally dark in colour from the decomposition of organic matter. The A-horizon (aka as topsoil) is also dark with organic matter and is a zone of generally loose and powdery sediment. Rainwater from the surface leaching through the topsoil dissolves various minerals and nutrients and moves them down through the ground into the B-horizon or subsoil. Most of the leached materials stop and accumulate in this zone. Subsoil is usually lighter in colour, lower in organic material, and more densely packed. The C-horizon is the transition zone where the breakdown of the parent material is initiated. Beneath the C-horizon is the unaltered parent material (bedrock or sediments). Soil chemistry and a variety of physical processes, along with plant and animal activities, dissolve and break down the parent material, changing rock into sediment and sediment into soil. Size is the most important characteristic of the particles that make up a body of sediment. Gravel, sand, silt, and clay are the major categories of sediments. Gravel, sand, silt, and clay particles are defined primarily by their size. Gravel is larger and very coarse ranging from pebble to boulder size. Sand is gritty to the touch and the individual grains can be seen with the naked eye. Silt is finer and the individual particles can only be seen with a microscope. Silt is smooth and slippery to the touch. Clay is extremely small and particles can only be seen with the very high magnification of an electron microscope. Clay is sticky and plastic when wet. Soil scientists use the percentage of three components – sand, silt, and clay – to define the texture of soils. Organic material in soil, or humus, may be of plant, animal, or microbial origin and be relatively fresh or highly decomposed. Living organisms also inhabit the soil. The organic portion of sediment is reported as a percentage and determined by weighing a sample before and after burning, which removes the organic component (Price and Burton 2011: 51-53).

Gravel	>2.0 mm
Boulders	>256 mm

Cobbles	64–256 mm (baseball size)
Pebbles	2–64 mm (US quarter)
Sand	0.10–2.0 mm
Very coarse sand	2.0–1.0 mm
Coarse sand	1.0–0.5 mm
Medium sand	0.5–0.25 mm
Fine sand	0.25–0.10 mm
Very fine sand	0.10–0.05 mm
Silt	0.05–0.002 mm
Clay	<0.002 mm

Table No. 4. Categories of sediments and size criteria (Price and Burton 2011: 53)

Sediments can provide answers to archaeological questions concerning the use of natural resources, environment and climate, settlement activity, technology, and construction. Sediments play a number of different roles in archaeological contexts: (1) as raw materials for pottery and building materials, (2) as a surface for the living places of past peoples, and (3) minor uses such as a binder for pigments, or for medicinal or cosmetic purposes. Clay was commonly used for making pottery in prehistory. Silts are sometimes used in ceramics and are a basic component in building materials such as mud daub, mud bricks, adobe, and fired brick. Sods, soil, and other sediments were used in the construction of earthworks by prehistoric peoples for walls, tombs, and other monuments. Human settlement is almost always found on sedimentary deposits. Humans dig and build and move these sediments around. They also leave physical and chemical traces of their activities in the ground. The physical traces are the visible remains of pits and posts, earthworks and foundations that remain. The chemical traces are the invisible deposits of elements and molecules left behind by various kinds of activities. Phosphate often marks places of human residence from the concentration of bone, excrement, and other materials that accumulate. Human activities of various kinds leave distinctive chemical traces that can be analyzed to determine what took place. The archaeological chemistry of soils and sediments is an important area of study because of the variety of information that these materials contain. Soils from prehistoric occupations may contain information on site extent, boundaries, activities, chronology, resource availability, or past environments. The chemistry of soil is remarkably complex, useful data have been obtained from a number of different elements (Price and Burton 2011: 54-55).

Metals

Metals are substances that have electrons freely distributed throughout the material, in contrast to other materials that have local chemical bonds in which electrons are shared only with adjacent atoms. In metal atoms can move past one another without breaking bonds thus pieces of most metals can be easily bent and shaped without fracturing. Both this ductility and metallic appearance are unquestionably key attributes that attracted early human interest. Most elements, in their pure "elemental" form are metals. But almost all elements are also quite chemically reactive and thus not found naturally in their elemental form. Metals that do occur naturally as pure elements include the "noble" metals, so-called because they are not chemically reactive, i.e., gold, silver, platinum, and rare "platinum-group" metals such as osmium and iridium, and copper. Copper is more reactive and more common and thus sometimes called a "base" metal. Copper must have been an attractive and useful material to prehistoric peoples. The earliest examples of copper are in the form of pendants and jewellery. Several other elements, including tin, lead, and zinc, occur in nature in elemental form, as do natural alloys of some metals such as osmiridium (osmium + iridium) and awaruite (nickel + iron). However, such occurrences are extraordinarily rare, found only in unusual geological contexts, and are normally in quantities too small to be noticed, much less broken. Native copper is commonly associated with other copper minerals: the bright blue azurite and bright green malachite, both of which are copper carbonates, and various sulfides and arsenate compounds that are the primary ores of copper today. Heating these minerals in an oxygen-starved atmosphere (e.g., with excess charcoal) reduces them to metallic copper. More importantly, the inclusion of arsenic containing copper sulfide yields copper in which some arsenic is dissolved. When arsenic mixes with copper, the resulting alloy has a lower-melting point than copper, flows better at high temperature, is easier to work, and produces a harder, less brittle metal, i.e., arsenical bronze. This discovery is of no small importance, and marks the transition from the Stone Age to the Bronze Age. Much of the current interest in metals focuses upon lead isotopes. Although lead is not an essential component of bronze, it commonly contains several tenths of a percent of lead, probably through the accidental inclusion of lead bearing copper ores. Lead has four abundant isotopes: 204, 206, 207, and 208, the ratios of which vary geographically. Once metal technology developed to the point that high temperatures could be attained in an atmosphere deficient in oxygen, other metals such as zinc, tin, lead, and iron could be produced. The Iron Age, the sequel to the Bronze Age (and which actually overlaps the Bronze Age by a millennium) began sometime in the late second millennium B.C. Because metals in ordinary petrographic thin-sections are opaque, they are studied by using direct, reflected light instead of transmitting light through the sample. The metallographic microscope is similar to the transmitted light, petrographic scope except the illuminator is placed above a polished sample, rather than below it, and polarized light shines directly down on the sample. By observing characteristic textures and subtle changes in colour and brightness when the sample is rotated in polarized light, an experienced petrographer can identify native metals, metal ores such as oxides and sulfides, and alloys. Chemical analyses can be used, but for most metals one needs only to know the major elements such as copper and tin. Chemical identification of metals does not require either high precision or trace sensitivity. X-ray fluorescence has often been used in metal identification and has recently been developed into portable, non-destructive devices for field and museum use. X-ray diffraction can identify metals structurally, but this can be complicated by more than one compound in complex alloys such as steel (Price and Burton 2011: 55-57).

Metal	Chemical Symbol	Abundance in earth's crust(ppm)
Copper	Cu	70
Gold	Au	0.005
Iron	Fe	50,0000
Lead	Pb	16
Mercury	Hg	0.5
Silver	Ag	0.1
Tin	Sn	40
Zinc	Zn	132

Table No. 5. Metals (Goffer 2007: 154)

Other Materials

Some other important materials are given as follow that can be obtained from archaeological sites.

Glass

A glass is a material that is solid but resembles a liquid in that its molecules are randomly oriented, without any crystalline structure. This comes about by cooling liquid so quickly that the molecules lose their energy to move around before they have time to link together into any regular arrangement. Although other substances can be chilled to produce solids without crystalline structure, here the term glass means the common parlance to mean glass made predominantly of silica (SiO_2), whether natural or man-made. Because glass molecules are randomly oriented, without an extensive network of chemical bonds, they do not interact strongly with light – and thus are translucent or transparent. Pure silica melts at approximately 1,700°C, a temperature not possible prehistorically or in nature. The presences of other elements, especially the alkali elements those in the first column of the periodic table markedly reduce this melting point. Elements in the second column known as the alkaline earth elements tend to raise the viscosity of molten glass, reducing the mobility of the atoms and making it harder for crystallization to occur. These elements tend to stabilize the glass during crystallization. Rocks that contain a lot of alkali elements such as sodium and potassium melt at temperatures less than 900°C. Even a trace of water in the mix can lower the melting point by another 100°C. If such a rock erupts at the surface of the earth and looses this water, its melting point rapidly rises and the rock can solidify into a natural glass like obsidian. Thus most obsidian has a composition of 70–75% silica, with 7–12% alkali oxides (Na_2O andK_2O) and 10–15% Al_2O_3.Such mixtures of silica and other minerals would have made it possible to produce glass in antiquity by lowering the required melting temperatures. The earliest known glass comes from Egypt and the Near East from approximately2500 B.C when pyrotechnology had developed to the point that bronze could be smelted at temperatures well above 1,000°C. The first glass objects were beads, perhaps initially produced as by-products of metal-working slag or during the manufacture of faience, a pre-glass vitreous material made by a process similar to glazing. Faience, or Egyptian faience, is anon-clay-based ceramic, made from sand, salt (natron), calcite lime, and mineral colouring, displaying surface verification which results a bright luster in various colours. The first glasses were made by mixing silica-rich sand with alkali-rich plant ashes or naturally occurring alkali-rich minerals, along with some lime, either as natural material in the sand or as deliberately added limestone. Thus a lot of early glass has compositions a lot like that of obsidian, i.e., about 70% silica, 15%Na_2O + K_2O, and 10% CaO + MgO. Most glass produced today still has this basic"soda-lime" composition. Early glass artefacts were solid and used as jewellery because of their beauty and value. The oldest fragments of glass vases (hollow glass objects) date back to around 1500 century B.C and came from Mesopotamia. Once the basic recipe for making glass was established, additional components were added to refine its properties, especially colour. Early raw materials for glass often included small amounts of iron, which imparted an unwanted brown or green appearance. Other minerals could be added to produce richer colours. For example, cobalt produces a deep blue while uranium develops a bright yellow colour. More compounds could be added to change the luster and opacity. Glassblowing began only at the end of the first century B.C. Blowing glass inside olds sped up the production process and greatly increased the variety of shapes and designs that were produced. The Romans expanded the glass industry substantially and their cups, bottles, pitchers, and vases of glass were found across Europe and around the Mediterranean. With their conquest of Egyptian glass production centres in Alexandria, Egypt, and Sidon, Syria, the Romans took glassmaking to an art form not rivalled until modern times. Thus compositional studies have some value in identifying the regional production centres for glass artefacts that find themselves a long ways from home (Price and Burton 2011: 59-62).

Pigments and Dyes

Mineral	Colour	Composition	Note
Hematite	Red	Fe_2O_3	The pigment responsible for the colour of red ochre. Very

			widely used as a ceramic pigment
Magnetite	Black	Fe_3O_4	Common ceramic pigment. Can be made by firing hematite in oxygen starved (reducing) conditions
Goethite Limonite	Yellow/brown	FeO(OH)	The pigment responsible for the colour of yellow ochre
Cinnabar	Vermillion red	HgS	Unstable upon heating
Azurite	Deep blue	$CuCO_3$	Unstable upon heating
Malachite	Bright green	$CuCO_3$	Unstable upon heating
Sulfur	Yellow	S	Unstable upon heating
Orpiment	Orange-yellow	As_2S_3	Unstable upon heating Often with realgar and cinnabar

Realgar	Orange-red	As4S4	Often with orpiment and cinnabar Unstable upon heating
Chrysocolla	Turquoise blue	(Cu,Al)2H2Si2O5(OH)4 .*n*(H2O)	
Lazurite	Ultramarine	(Na,Ca)8(AlSiO4)6(SO4,S,Cl)2	Rare and highly valued in lapis lazuli
Calcite	White	CaCO3	
Gypsum	White	CaSO4.2H2O	
Kaolin	White	Al2Si2O5(OH)4	
Anhydrite	White	CaSO4	May be natural or formed by heating gypsum
Charcoal	Black	C	

Table No. 6. Common minerals used for preparation of colorants and dyes, colour, chemical composition, and additional information (Price and Burton 2011: 63)

Natural colorants can be conveniently divided into two categories: pigments, which are insoluble solids commonly of mineral origin, and dyes, which are normally used in liquid form and are commonly of organic origin. Pigments are used as paints and to create coloured surface treatments, e.g., to paint murals and to decorate pottery; dyes are mainly used to colour animal and plant fibers. Pigments and dyes are compounds that reflect light of specific wavelengths (colours) and are suitable for colouring other materials. These colorants can be either natural or synthetic (artificially made), soluble or insoluble, and organic or mineral in composition.

Colorants that are insoluble in water and usually inorganic are pigments. Organic colorants soluble in water are known as dyes. Most pigments of archaeological interest are minerals, although other materials such as charcoal and burned bone can also be pigments. Oxides of iron are among the most abundant and thus widely used pigments. Hematite, $Fe2O3$, the earthy red mineral responsible for the red colour of red ochre is the oxide of iron in its "oxidized" +3 state. Coarsely crystalline hematite is a shiny, black mineral but when crushed to particles of microscopic size, they are red. Hematite naturally occurs in many clays in this microscopic and can impart a red colour when present at levels as low as 1%. These hematite bearing clays are the material commonly used as red ochre. The hydrated form of iron oxide, $FeO (OH)$, limonite or goethite, can similarly be shiny black as a coarsely crystalline material but is brownish yellow when finely powdered and is responsible for the colour of yellow ochre as a pure material or in clay matrix. Magnetite, $Fe+2Fe2+3O4$, is a black oxide of iron that occurs in nature but is more likely produced by firing hematite-bearing pigments in an oxygen-starved environment, known as a "reducing" environment because it reduces the valence of some of the iron from +3 to +2. Conversely, firing a magnetite-bearing pigment in an oxygen-rich environment oxidizes the magnetite to hematite. This oxidation and reduction of iron, along with burning out carbon-rich organic matter, is responsible for the colours of many ceramic pastes, which normally contain several percent iron oxides. Copper is another common element that has many brightly colored blue and green minerals used as pigments. These are mostly hydrated minerals or carbonates, which decompose upon heating to temperatures, required by ceramics and thus, if applied to pottery, must be applied after firing. Other metals such as nickel and chromium are more rare but have similarly brightly colored blue and green minerals that can be used as pigments. Most pigments are strongly colored, fine mineral powders prepare by grinding solid raw materials. A few insoluble pigments of vegetable or animal origin are also known, from a certain kinds of tree bark, nut shells, and animal horn. Because pigments are insoluble, to apply them to the surface of a material, they are usually mixed with an adhesive binder, which could be a plant gum or resin, egg albumin, or other animal-derived adhesives. One of the earliest uses of pigment can be seen in the cave paintings of the Upper Palaeolithic in France and Spain, the oldest of which are dated to more 30,000 years ago. These pigments were likely mixed with a variety of binders such as egg white, mineralized water, and blood before being applied to the surface of thecae or rock. The use of portable Raman spectroscopy is greatly increasing the number of analytical studies of prehistoric art. This technique is non-destructive, can be done in situ, and provides a reliable indication of the pigments and binders that are used in the paintings. Dyes are normally organic, water-soluble and applied to organic materials such as textiles and fibers of animal or vegetable origin such as wool or cotton. Pigments and dyes are produced from a wide range of natural materials including plants, insects, and shellfish. The solubility trait of dye is essential for the colour to be fixed to the fibers of the textile and be resistant to repeated washing. There are two general methods for dyeing cloth and fibers. Vat dyeing refers to the process of dissolving the dye in water and soaking the cloth. When the material dries, the colour reconstitutes itself on the fabric. This method is often used with indigo dyes, which are largely insoluble without chemical reduction, usually fermentation in an alkaline solution. Mordant dyeing requires soaking fabric in a salt of iron or aluminium, prior to immersion in a dye suspension. A mordant is a substance used to set the colour on fabrics by forming an insoluble compound with the dye. Mordant dyes are usually based on plants and the colours of red, yellow, and purple are common. Both types of dyes can survive for several thousand years under favourable conditions. Thin layer chromatography (TLC) or high performance liquid chromatography (HPLC) is often used to try and identify visible natural dyestuffs. The principle component of dye is carminic acid which may be up to20% of the insect by weight. This acid produces a range of beautiful shades of red. Vegetal Red: These red dyes are found in the roots and beneath the outer skin of the various members of the Rubiaceae plant family. Vegetal Yellow: There are more than15 species of plants in South America that produce sources for yellow dye. The primary flavonoid components of these plants are luteolin and apigenin. Flavonoids, a class of plant secondary metabolites, are widely distributed in plants and fulfil many functions including producing yellow or red/blue pigmentation in flowers. Luteolin and apigenin are most often found in leaves and flowers of plants. Vegetal Blue: The blue or purple colour indigo is commonly derived from a plant known as Isatis tictoria or various Indigofera species. This was obtained from the plant leaves which were soaked in water and fermented to convert the glycosideindican in the plant to the blue dye idigotin. The precipitate from the fermented leaf solution was mixed with a strong base such as lye, pressed into cakes, dried, and powdered. The powder could be mixed with various other substances to produce different shades of blue and purple. The colour indigo, now produced synthetically, is used in the production of denim cloth for blue jeans. Tannins: from many species of plants, found in the vacuoles or surface wax of the plants. Tannins were used to produce brown to dark brown colours. Tannins are astringent, bitter plant polyphenols that either bind and precipitate or shrink proteins. Tannins are also an important ingredient in the process of tanning leather. Complex chemical degradation of dyes and fibers takes place during both burial and museum storage contexts. When a fabric has completely lost its original colour, the analysis is more complicated. For badly faded textiles, a different analytical path is involved, searching not for the dyes themselves but their detectible degradation products (Price and Burton 2011: 62-66).

Concretes, Mortars, and Plasters

Concretes, mortars, and plasters are composites used primarily as building materials. Concretes are used to create an artificial, shaped stone. Concrete is a composite made up of cement, a fine aggregate such as sand, a coarse aggregate such as gravel, and water. Cement is a binding agent, usually including finely powdered burnt lime. There are two types of cements, non-hydraulic cements which set in air, and more durable, hydraulic cements which can set under water and are largely insoluble. Mortars are used to fill the gaps between blocks and bind them together in construction. Mortars generally contain other aggregates smaller than 5 mm in diameter; concrete has larger inclusions as part of its composition. Plasters are another composite material used to cover and protect exposed surfaces. Plasters are generally fine-grained materials than can be used to create a smooth finished surface. Lime (CaCO3) is a common material used for making hard and water-resistant cement. It is found in many parts of the earth as a component of limestone. It can be chemically altered by heating to produce stronger binding agents and it can breather easily ground to a fine powder. Lime burned at 900°C turns into quicklime (CaCO3), which can be combined with water in the absence of carbon dioxide to produce slaked lime (Ca (OH) 2). This wet mass sets slowly with the loss of water to produce interwoven crystals of Ca (OH) 2 and then combines with carbon dioxide in the air to produce lime. The major element composition of the geological samples can be determined by XRF and SEM (Price and Burton 2011: 66-67).

Shell

Shells are occasionally found in archaeological sites, both naturally and as a by-product of human activity. Shellfish – such as oysters, clams, mussels, scallops, limpets, and many others –

are an important category of foods eaten both today and in the past. Evidences for the consumption of shellfish dates back to several hundred thousand years in human prehistory. Shellfish are a plentiful and easily collected source of protein and essential trace elements such as iron, copper, and magnesium. Shells from both fresh and saltwater species appear in archaeological sites. Shellfish belong to the biological group of species known as molluscs, animals with a shell and a foot. Univalve molluscs have one shell and include many species of snails, conchs, and others. Bivalve molluscs have two shells and include clams, scallops, and oysters. There are many species of molluscs and both freshwater and salt water varieties. In addition to their use as food, shells were often used to make beads, fishhooks and other objects. Large heaps of shells, known as shell middens, representing the accumulated refuse from thousands of meals can be found on coasts and river banks in various parts of the world. These shell middens can be enormous, hundreds of meters long, tens of meters wide, and up to 15 m high. Careful preparation and study of these shells can help determine how old the creatures were when they were harvested. In addition to information about diet and seasonality, shells at archaeological sites provide information about the local habitat and climate change. Different species of shellfish live in different depths of water, and prefer different temperatures, salinity, and amounts of current. Shells are composed of calcium carbonate (CaCO3) which is a molecule composed of calcium, carbon, and oxygen. The exact ratio of oxygen isotopes in shell depends on the temperature of the water in which the shell formed. Determination of that ratio in the shell can provide information on changes in water temperature (correlated with air temperature) over time. That information can be used to estimate where along a coast the shell is coming from (Price and Burton 2011: 68-69).

Methods of Analysis

Analytical chemistry is used for the analysis of archaeological materials. Analytical chemistry is often described as the area of chemistry responsible for characterizing the composition of matter, both qualitatively (what is present) and quantitatively (how much is present). This description is misleading. After all, almost all chemists routinely make qualitative or quantitative measurements. The argument has been made that analytical chemistry is not a separate branch of chemistry, but simply the application of chemical knowledge (Harvey 2000: 2).

Analytical method	**Single element**	**Multiple Elements**	**Molecules**	**Surface Composition**	**Crystal Structure**
Gravimetry	✓	✓	-	-	-
Volumetry	✓	✓	-	-	-
Chromatography	-	-	✓	-	-
Electrochemistry	✓	✓	✓	-	-
Electron probe microanalysis	✓	✓	-	✓	-
Mass spectrometry (MS)	✓	✓	✓	-	-
Nuclear activation analysis	✓	✓	-	-	-
Spectroscopy					
Emission spectroscopy	✓	✓	-	-	-
Absorption spectroscopy					
Infrared	-	-	+	+	✓
Fourier transform infrared	-	-	✓	-	-
Raman	-	-	✓	-	-

Ultraviolet	✓	✓	-	-	-
Visible	✓	✓	-	-	-
Auger spectroscopy	✓	✓	-	✓	-
Thermal methods	-	-	✓	✓	-
X-ray technology					
X-ray diffraction	-	-	✓	-	✓

Table No. 7. Methods of Chemical Analysis and Their Uses (Goffer 2007: 32)

Analytical chemistry is based on five-step process:

1. Identify and define the problem.

2. Design the experimental procedure.

3. Conduct an experiment, and gather data.

4. Analyse the experimental data.

5. Propose a solution to the problem (Harvey 2000: 5).

Archaeologists use many different kinds of tools, from shovels, trowels, and brushes to mass spectrometers and atomic reactors. Laboratory archaeologists employ wide range of equipment and instruments. They also use a lot of abbreviations. Five common types of instruments in laboratories of archaeological chemistry are described here, each based on different principles: (1) microscopes, including a scanning electron microscope (SEM) (2) spectroscopic and spectrometric methods, including inductively coupled plasma/mass spectrometry (ICP-MS), (3) neutron activation analysis (NAA) using a nuclear reactor, (4) X-ray diffraction (XRD), and (5) molecular analysis using gas chromatography (GC) and mass spectrometry (MS). These instruments can determine the composition of many kinds of archaeological materials. Each has advantages and disadvantages and each provides specific kinds of information about the material that is analysed. Instrumentation for chemical analysis can be conveniently divided into (1) methods for elemental and isotopic analysis that measure amounts of individual atomic components such as phosphorus and iron and their relatives, and (2) methods forth molecular analysis of organic materials that identify compounds such as dyes and animal fats. This distinction reflects the long-standing division between inorganic and organic analysis in the field of chemistry. Instruments known as spectroscopes or spectrometers are generally used for elemental analyses. Spectroscopic methods examine the interaction between atoms and light and are defined primarily by the portion of the electromagnetic spectrum that they use. Instead of the spectrum, more powerful mass spectrometers use electromagnetic fields to sort atoms according to their weight. Specific atomic weights, or masses, correspond to specific elements and isotopes. For the molecular analyses of organic compounds, differences in the physical properties of molecules are helpful in identifying them. These "chromatographic" methods are defined by specific properties, such as volatility and solubility, which are used to separate individual compounds. Such separation methods are commonly used in combination with mass spectrometers to sort and identify molecules by their weight. Inorganic mineral compounds – for example, jadeite, turquoise, and many others are defined by their crystal structure as well as by their elemental composition. Analysts use the petrographic microscope and XRD to reveal crystalline structure and infrared (IR) spectroscopic techniques to revealing the kinds of chemical bonds in the crystal. From this information individual minerals can be identified (Price and Burton 2011: 73-74).

Magnification

The optical microscope is one of the less expensive and complicated tools in the archaeometric lab. Little training is required for use and operational costs are minimal. It is much easier to maintain, at much lower expense. Usually an entire artefact can be examined, and the process is totally non-destructive. Moreover, many microscopes are portable. Plant pollen, seeds, pottery, stone tools, bone, textiles, metalwork, and many other materials can be studied under a microscope. Microscopes are used for the detailed examination of the surfaces of archaeological objects and provide visual information through magnification. The microscope is commonly used to identify small particles such as bits of charcoal and shell. Important authentication studies have depended on microscopic observations of tool marks, pottery provenience through the recognition of ceramic tempers, and many other kinds of evidence. Microdebitage (tiny debris produced by human activity and deposited in archaeological contexts) provides data about technology and function; observations of seeds, pollen, phytoliths, and bone debris can inform us about diet. Experienced microscopists can easily identify many substances and provide important new information. Two general kinds of microscopes are employed in archaeological studies, optical microscopes and electron microscopes. More complicated electronic microscopes, including the SEM, the scanning tunnelling microscope(STM), and the atomic force microscope (AFM) can be used for measurement of the elemental composition of materials under analysis (Price and Burton 2011: 74-75).

Optical Microscopes

An optical microscope uses lenses at the ends of a hollow tube to magnify an object. The same principle is found in a telescope. Optical microscopes are often used in the range of 5–100×, but complicated models can magnify image up to 1,000×. A light source is used to illuminate the object of study on a platform beneath the microscope tube. The light source is commonly above the object. Standard, single-tube optical microscope has no depth in the field of view. A binocular microscope, with two independent tubes focused on the same object, magnifies in three dimensions. The large, bright stereoscopic field of the binocular microscope is ideal for examining a variety of archaeological materials including plant remains, small artefacts, usewear, and cut marks (Price and Burton 2011: 75-76).

Scanning Electron Microscope

SEM is an awesome instrument capable of extremely high magnification (25,000×compared to 1,000× for optical microscopes). The SEM in provides a sharp image with pronounced shadows, producing a distinctly three-dimensional aspect. This makes the SEM superior to optical microscopy for identifying microscopic grains such as seeds, spores, and pollen and for studying in high detail microscopic features such as the grooves made by tools and animal teeth. The SEM is widely used in archaeology to obtain high-resolution images of artefacts and other materials. A SEM can reveal features of materials like plant remains or stone tools that are otherwise invisible. Magnifications available on an SEM have an enormous range, commonly from about 25 to 250,000×. The SEM creates magnified images using high-energy electrons, instead of light waves. Such electrons behave like light waves except they have much shorter wavelengths and can be used to examine smaller objects than can be seen with an optical microscope. A sample is placed inside the vacuum chamber of the instrument and the air is removed. An electron gun fires a beam of electrons at the sample. This beam passes through a series of magnetic lenses that focus the electrons on a very small spot. As the electron beam hits the sample, secondary electrons are knocked loose from its surface. A detector counts and amplifies these signals for the computer and that provides the three-dimensional image of the object surface on a monitor. An SEM can also provide high resolution compositional information by examining prepared flat surfaces on an object. If a sample such as a potsherd is ground and polished to a shiny, flat surface, then the number of electrons reflected, or "backscattered," from the surface can be recorded. This backscatter is proportional to the atomic density of the mineral being examined. Quartz (SiO_2), for example, has a lower atomic density than magnetite (Fe_3O_4) and appears much darker in a BSE ("backscatter electron") image. In this way, an SEM can be used to determine the mineral content of some materials, as well as providing greatly magnified imagery. Another aspect of the SEM of great utility to archaeologists is its capability to perform multielement analysis of a microscopic portion of a sample, a technique called "microbeam" analysis. For this analysis, one prepares a flat, polished surface, free of surface topography. The sample, a centimetre or two in diameter, is first cut with a saw to obtain a flat surface. This is then placed in a small cup with epoxy or another resin to make a resin plug with the flat surface exposed. The surface is then ground with relatively coarse abrasive to remove surface imperfections. Progressively finer abrasives are used to remove the scratches left by the previous abrasive until a nearly mirror-like finish is obtained. The surface is then coated very thinly with a conductive material such as gold or carbon, usually by electro-vapour deposition. Samples are placed in a vacuum chamber along with the conductive material that is heated until glowing hot. The conductive materials evaporated and condense as a thin layer on the sample surface. The plug is then ready to be placed in the SEM. Because the incident electron beam can generate X-rays that are diagnostic of the material under the electron beam, one can obtain a quantitative analysis of the major elements, and minor elements as well if present with a precision of a few tenths of a percent or more. It is not highly sensitive for trace element work below hundreds of parts per million, however. The analyst should also be aware that, while the electron beam might be focused on a spot less than a micron across, X-rays can be generated from a much bigger volume several microns deep, so that the analysis might be sampling a bigger region than is visually apparent. This can be a factor in ceramic analysis – analyses of mineral grains that are hundreds of microns across might be accurate, but a clay paste with submicron particles typically has high and, on a micron scale, variable porosity. Clays can even be mineralogically heterogeneous on such a scale, so that microbeam analyses must be carefully checked for consistency. Other detectors, such as for cathodoluminescence, can be mounted in the SEM that can reveal additional compositional information (Price and Burton 2011: 76-78).

Elemental Analysis

Elemental analysis involves measuring the composition of materials to determine the presence and amount of various elements and is a fundamental aspect of almost all chemistry. It is a predominant part of archaeological chemistry and has widespread applications. Elemental analysis has been employed in archaeological studies for more than a century. Virtually all kinds of archaeological materials have been studied in some way or another using elemental analysis. Elemental analysis can perhaps be best understood in terms of the history of its development. Today scientific equipment has progressed to the level that instruments measure not only elemental abundances, but also their isotopic ratios, providing entirely new dimensions of inquiry in archaeological chemistry (Price and Burton 2011: 78-80).

Spectroscopy

Spectroscopy, the study of the interaction between matter and electro-magnetic radiation, provides a wide range of analytical methods. The energy of all atoms and molecules is discrete when atoms or molecules interact with (absorb or emit) radiation, a type of energy, they do so in a distinct manner characteristic of a given composition. This means that when they absorb or emit electromagnetic radiation, each type of atom and molecule does so at well-defined wavelengths. Detecting and measuring the spectroscopic characteristic of material provides, therefore, a powerful tool for the study of their composition and structure. Since the form of interaction of different types (infrared, visible, ultraviolet, X rays) of electromagnetic radiation with materials is different, spectroscopic studies also yield information on a variety of other characteristics of the materials (Goffer 2007: 34).

More common methods for elemental analysis to determine the elemental contents of a sample include spectroscopy and spectrometry. Spectroscopy measures changes in atoms that cause a specific light photon to be either absorbed (absorption spectroscopy) or emitted (emission spectroscopy). This light has a precise wavelength or energy, characteristic of a specific element in the periodic table. The simplest (and oldest) form of elemental analysis was not spectroscopic, in fact, but colorimetric. This method was based on the reaction of a strongly colour chemical in a solution. The appearance of a specific colour in the solution revealed the identity of the element of interest. If the colour intensity is proportional to the amount of that element present, the method can also be used to estimate the amount of the element present. One colorimetric technique still in use in archaeology is a field test for soil phosphate. Phosphate in soils and sediments is an indicator of past human activity. Phosphate testing of soil samples is used to look for such indications. Small sample of soil is mixed with hydrochloric and ascorbic acid to release soluble phosphates. The reaction produces a distinctive blue colour in the presence of phosphate and the intensity of the colour reflects its concentration. Results can be determinedly eye or with the use of an instrument. Colorimetric tests are not possible for many elements, however, and in some cases several elements can produce the same reaction. More refined methods have replaced colorimetric techniques, using other parts of the electromagnetic spectrum. Even the spectroscopic techniques, however, rely upon the same principle, that a particular part of the spectrum can be used to measure the amount of specific element in a sample. A simple colorimetric spectrometer provides a good example for the operation of more complicated techniques. The instrument employs a lamp, a monochromatic(a device, either a prism or a diffraction grating, to disperse light from the lamp into a spectrum), a slit through which a particular colour can be selected, a sample through which the light of a specific colour passes, and a photosensitive detector that measures how much light passes through the sample. Hundred present of the light is transmitted through the instrument if the sample solution is clear; none is absorbed. With increasing intensity of a colour in the solution, less light is transmitted, more is absorbed, and the amount absorbed can be measured. The amount of an element in a sample is determined by comparison to a known reference material. The intensity of the radiation being absorbed or emitted is measured for a set of samples of the reference with known concentrations of the element of interest. More complex instruments, used for atomic absorption spectroscopy, are similar to the simple spectrometer but they measure absorption from the behaviour of atoms, not colour intensity. Atomic absorption is often called “flame AAS.” The sample is normally in a solution that is sprayed into a flame that atomizes the sample (i.e., it breaks the sample down into individual atoms). The atoms are introduced into the flame in their low-energy state and can be excited to higher energy state by absorbing a photon of a specific wavelength, ordinarily in the visual part of the spectrum. This photon is provided by a lamp in the instrument that emits precisely the required wavelength. To measure calcium, for instance, a lamp with a calcium filament, with the exact wavelength needed for calcium, shines through the flame with the sample. A detector records how much calcium light is absorbed by the sample, which is proportional to the amount of calcium in the solution. Other elements can be measured in the same way using the appropriate elemental light sources. Newer instruments, however, utilize "emission" methods. They use different techniques for exciting atoms into a higher energy state and then measure the photons emitted by the excited atoms, rather than requiring a variety of lamps and measuring absorbed light. Both optical emission and absorption methods are best suited for elements that are easily atomized and have a spectrum in the visible range, i.e., those elements in the first and second columns of the periodic table and the transition metals. By including the ultraviolet portion of the spectrum, a few additional elements can be added – phosphorous, for example, is an important one for archaeological studies of soils. The results from most types of elemental analysis today are values for the elements selected for measurement in parts per million or parts per billion depending on the resolution of the instrument in use (Price and Burton 2011: 81-84).

Inductively Coupled Plasma-Optical Emission Spectrometer

The most common type of emission spectrometer in use today (inductively coupled plasma-optical emission spectroscopy, or ICP-OES) atomizes a sample by passing an electric current into a gas plasma that contains the sample. In these optical emission methods, the sample is heated to high temperature. At this temperature the individual elements glow with their representative colours, e.g., red for potassium, yellow for sodium. The light from the sample is focused on a monochromatic to select a wavelength appropriate for the element of interest. That light at the correct wavelength is focused on a detector that measures its intensity. Emission spectroscopy is used to measure concentrations of a wide range of elements. Complex mixtures of elements heated to high temperature display characteristic emission spectra composed of multiple monochromatic lines – the sum of the spectra of the individual elements. When the light is separated into individual spectral lines by the spectrometer, each element is represented by several lines and the pattern of these lines is unique to that element. The intensity of the light indicates the amount of an element present in the mixture. This principle provides for the quantitative recording of elemental abundance. Ideally, an emission source should atomize a sample completely and provide actable signal over a wide range of concentrations. Argon plasma comes close to this ideal. Argon plasma is a hot, gaseous fountain of atoms, ions, and electrons, held in place by a magnetic field produced by a radio frequency induction coil. Radio frequency energy is inductively coupled with the plasma, creating an immense number of argon ions and electrons along with intense heating. The resulting discharge reaches temperatures of 8–10,000 K, the temperature of the surface of the sun, which will atomize and excite even the most difficult refractory samples. Traditional excitation sources included combustion flames, arcs, and sparks. Flames are limited by relatively low temperatures so that it is difficult to analyze refractory elements or elements with high excitation energies, particularly at low concentrations. In addition, combustion products and flame gases cause both chemical and spectral interferences. Arcs and sparks are capable of higher temperatures, but are strongly affected by the nature of the sample. Minor variations in sample composition can cause variation in the excitation conditions, requiring a close matching of samples and standards or the use of an internal standard. Argon plasma offers a number of advantages as a source for emission spectroscopy. Argon is an inert gas and will not react with the sample so chemical interference is greatly reduced. At plasma temperatures, atomization is complete and elemental spectra do not reflect molecular components. Detection limits are high for most elements. Accuracy and precision are excellent. In addition, ICP/OES requires less sample preparation and less sample amount than other techniques.ICP/OES can be conducted either simultaneously or sequentially. Simultaneous instruments rely on a polychromator or direct-reading spectrometer to read up to60 elements from the same sample excitation. Sequential analyses use a computer controlled, scanning monochromator system. The light emitted by the sample in the plasma source is focused on the entrance slit of the monochromator and the spectrum is scanned through the region of interest. Typically, it is possible to determine several elements per minute in the sample in a sequential pectrometer. The results from most types of elemental analysis today are values for the elements selected for measurement in parts per million or parts per billion depending on the resolution of the instrument in use(Price and Burton 2011: 84-85).

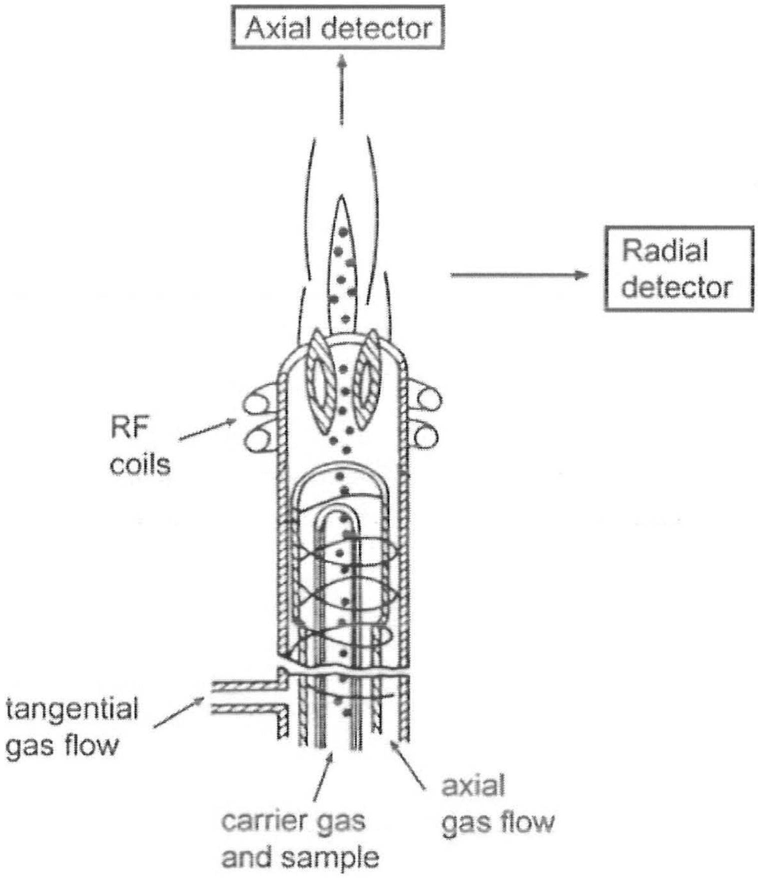

Figure 5: Schematic diagram of an ICP torch. The sample is carried into the torch by the carrier argon gas, and is ignited by radio-frequency heating from the RF coils. The tangential argon flow lifts the flame from the burner, preventing melting. The position of the detector in axial or radial mode is shown (Pollard et al. 2007:58).

X-Ray Fluorescence Spectroscopy

X-Ray fluorescence analysis (XRF) has developed into a well-established multi elemental analysis technique with a very wide field of practical applications, especially those requiring non-destructive analytical methods (Beckhoff et al. 2006: 1). The history of elemental analysis has seen a gradual shift from the use of visible light to the invisible parts of the spectrum. X-ray fluorescence spectroscopy (XRF) is similar to optical emission spectroscopy, but X-rays rather than electric currents are used to excite atoms. Unlike absorption methods, in which the incoming photon must have a precise wavelength, XRF is an emission method; the incident photons are used to excite the atom to fluoresce. This technique is similar to using an ultraviolet light (higher incident energy) to cause materials to glow (fluoresce) in the visual spectrum (lower emitted energy). In XRD, distinctive "secondary" (or fluorescent) X-rays are emitted from a sample that has been excited by bombarding it with high-energy X-rays or gamma-rays. There is a characteristic X-ray diagnostic for each element. The intensity of emitted X-rays of a particular energy can then is measured to determine the abundance of that particular element. In contrast to most spectroscopic techniques, which generally require the sample to be in solution, XRF can be used on solid samples, normally as a powder. XRF is useful for archaeological materials such as ceramics and stones. XRF can sometimes be used in a non-destructive way, and today there are portable XRF instruments that can be carried into the field. X-ray spectroscopy is also a useful tool when used in combination with a SEM. The SEM uses very short-wavelength, high-energy electrons, commonly exceeding 15,000 v, to stimulate X-ray emission much as an incident X-ray beam would. When an X-ray detector is coupled to an electron microscope, a compositional analysis of very small areas, only a few microns wide, is possible. One application is the identification of the mineral grains that are found in complex materials such as prehistoric pottery, which is particularly useful for identifying small mineral grains in complex matrices such as tempered pottery(Price and Burton 2011: 86-88).

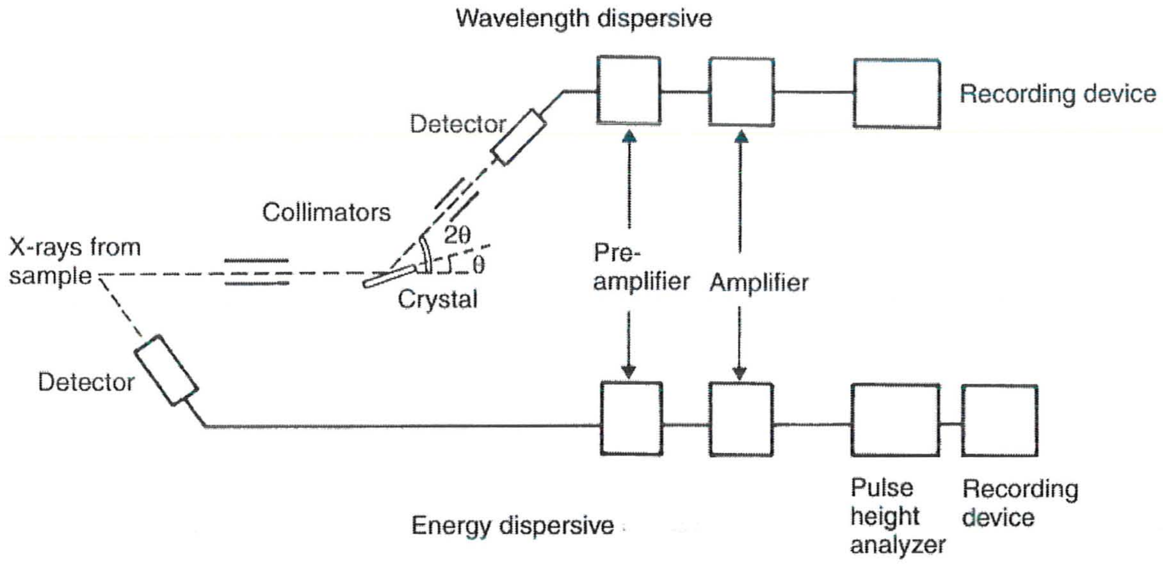

Figure 6: XRF (Pollard et al. 2007:58)

CN Analyzer

There are several instruments for elemental analysis that run on principles other than spectroscopy and that are designed for one or a few specific elements. One such instrument sometimes used in archaeological chemistry is a CN (carbon and nitrogen) Analyzer (aka a Carlo-Erba analyzer) and more advanced versions that measure CHN or CHNS or CHNSO (carbon, hydrogen, nitrogen, sulfur, and oxygen).These instruments are designed for the simultaneous determination of total carbon and nitrogen (and the other elements – hydrogen, sulfur, and oxygen) in wide range of sample types, both organic and inorganic. The sample is weighed into a tin container and moved to the combustion chamber at1, 020°C. Combustion of the tin container causes a powerful reaction in an atmosphere of enriched oxygen, completely oxidizing the sample. The combustion products (CO2, N2, NOx, and water) first go through an oxidation catalyst in the combustion chamber and then pass through a reduction reactor which contains metallic copper heated to650°C. Excess oxygen is removed and the nitrogen oxides are reduced to elemental nitrogen. The nitrogen, CO2, and water then move to magnesium per chlorate tube that removes the water. Nitrogen and carbon are separated by a chromatographic column and moved to a thermal conductivity detector that measures the concentrations of the two elements. The repetitive analysis of known standards under the same conditions is used to calibrate the instrument and quantify the amount of nitrogen and carbon. The ratio of carbon to nitrogen in a sample is used as a measure of the quality of preservation in bone and a means to determine if samples are reliable for the analysis of collagen for radiocarbon dating and dietary analysis using light isotopes. The ratio of C: N in living bone is 3.2; a ratio between 2.8 and 3.5 has been suggested as indicative of fossil bone sufficiently well preserved for analysis (Price and Burton 2011: 88-89).

Neutron Activation Analysis

One of the more widely used techniques of the last 50 years has been NAA, sometimes defined as instrumental neutron activation analysis (INAA). NAA uses gamma-rays, the highest energy end of the spectrum, to measure a wide variety of elements to parts-per-million concentrations. At the same time, NAA requires a nuclear reactor not readily available to many researchers.NAA is gamma ray spectroscopy that uses the slow "thermal" neutrons from nuclear reactor to excite the nucleus of an atom. When an atom absorbs a thermal neutron, its atomic mass increases by one and the nucleus becomes unstable. One or more nuclear reactions then take place that release gamma rays with energies characteristic of the particular nuclear decay reactions, along with other radiation. While the gamma-ray wavelengths are characteristic of particular elements, the intensities of these characteristic gamma rays are proportional to the number of atoms undergoing the decay process. Typically, gamma ray intensities are measured shortly after irradiation (after a few days) for short-lived decay processes and again after a few weeks to measure decay processes with longer half-lives. A large range of elements can be measured with good precision. NAA requires a powdered sample and is useful for materials such as pottery, the major archaeological application of NAA, and obsidian (Price and Burton 2011: 89-90).

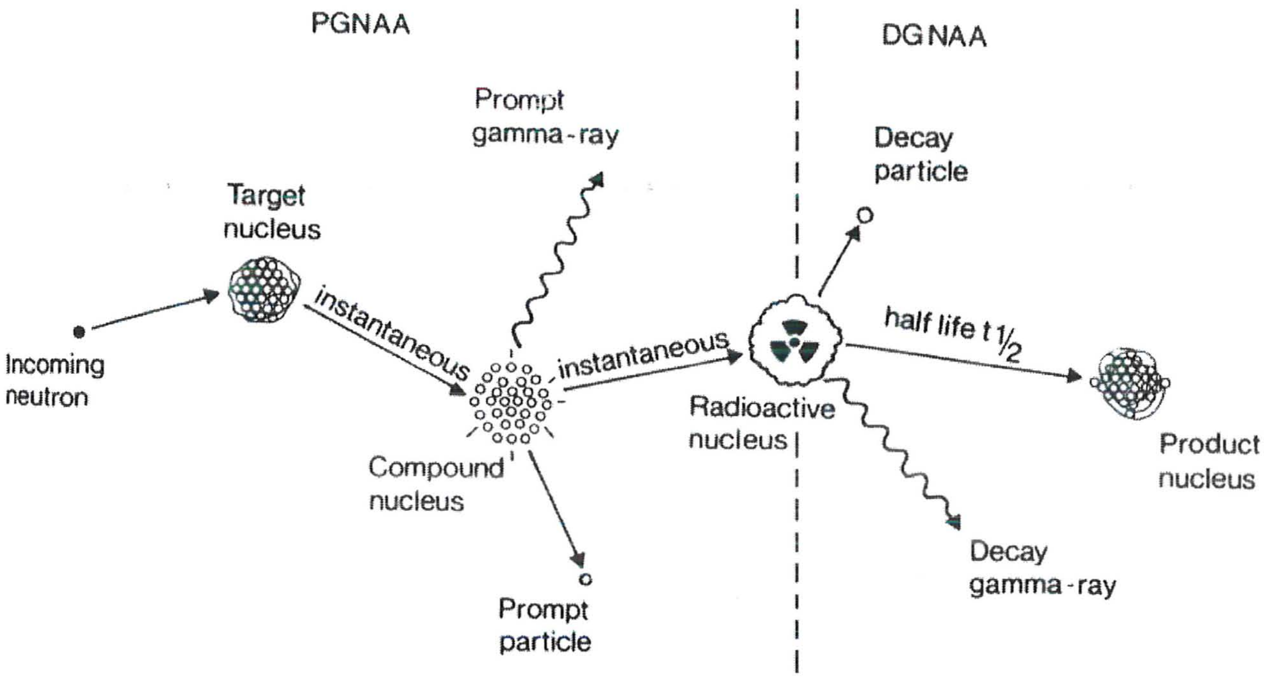

Figure 7: Schematic diagram of the nuclear processes involved in NAA (Pollard et al. 2007: 125)

Isotopic Analyses

The Scottish chemist Frederick Soddy first used the term isotope to describe his observation than atoms with different atomic masses have the same chemical properties and occupy the same position in the periodic table. The number of protons in the atomic nucleus defines the chemical properties and the identity of an element, but there can be different numbers of neutrons associated with the same number of protons, resulting in the same element having several possible masses, or isotopes. Isotopes are involved today in virtually all areas of chemistry. The use of isotopes in archaeological chemistry is widespread and rapidly growing, with many different applications. Different isotopes are used with many different kinds of materials to answer a variety of questions. Isotopes of oxygen, carbon, nitrogen, and strontium isotopes are more commonly used in archaeological applications (Price and Burton 2011: 90).

Oxygen Isotopes

Oxygen isotopes are used in archaeology primarily to study ancient environments and to examine past human mobility. Isotope measurements are always reported as a ratio of one isotope to another, lighter and more common cousin. Ratios are used in order to standardize the value that is reported, regardless of the amount of material measured or the concentration of the element present. The ratio of oxygen isotope 18 to oxygen isotope 16 is often used to measure past climate because it is directly related to atmospheric temperature. Oxygen isotopes are used as a proxy for temperature in studies of marine sediments, ice cores, faunal remains, and other materials. The abundance of the two isotopes depends on temperature-related fractionation processes such as evaporation, condensation, and transpiration. During evaporation at the ocean's surface, the lighter isotope, 16O, is preferentially released into the atmosphere because of its higher vapour pressure. As moisture-laden clouds move inland, the heavier isotope (18O) precipitates preferentially and rain clouds become progressively depleted in 18O as they move inland. Polar and inland rain is lighter than tropical and coastal rain; summer precipitation is less depleted than winter precipitation. Since condensation is also dependent on temperature, further depletion of 18O occurs at higher elevations and latitudes. Evaporation of inland surface water and evapotranspiration of water by plants releases more of the lighter isotope (16O) into the atmosphere and concentrates the heavier isotope in surface water and plants. Because of higher rates of evaporation, surface water and plants in arid regions exhibit more enriched d18O values than moister regions.d18O values of precipitation are passed on to plants and animals living in that environment. Oxygen isotopes in humans come primarily from drinking water. Water from food and atmospheric oxygen are minor, secondary sources. Meteoric water (rain) is the primary source of drinking water. Oxygen isotopes in ancient human skeletal remains are found in both bone and tooth enamel. Samples for the analysis of human skeletal remains are normally taken from dental enamel due to conditions of preservation and resistance to diagnosis. Thehydroxyapatite mineral, a primary component of enamel, contains oxygen, in both phosphate groups (PO4) and carbonates (CO3). Phosphate and carbonate produce comparable results for oxygen isotope ratios, but fewer samples is needed for carbonate, preparation is less demanding, and results between laboratories are more comparable. Oxygen isotope measurements are reported as a ratio of 18O to 16O. This ratio (d18O) is reported relative to a standard, and expressed in parts per thousand. The standard used is commonly VSMOV (Vienna Standard Mean Ocean Water) for phosphate or PDB (PeeDeeBee dolomite) for carbonate oxygen. The results from the use of these standards differ but can be calibrated. Values using the VSMOW standard are generally negative and range from approximately 0‰ (PDB) to–90‰ (PDB), or +20‰ (SMOW) to –70‰ (SMOW), in continental waters (Price and Burton 2011: 91-92).

Carbon and Nitrogen Isotopes

Carbon and nitrogen isotopes in archaeology are used primarily in the study of past diet, but there are also important applications that concern past environments and human activity. Carbon and oxygen isotopes have been used in proveniencing to determine the source of marble and other forms of carbonate rocks. Carbon isotopes have been used as survey tool to locate the boundaries of ancient soils and determine the extent of certain types of vegetation. The isotopes of carbon (13C/12C) and nitrogen (15 N/14 N) are measured in bone collagen using a mass spectrometer. While the level of these elements in bone is under strict metabolic control, the ratio of the stable isotopes reflects the ratio in the diet. Values for d13C in human bone collagen range between approximately –5‰and –25‰. There are two primary sources of variation in 13C in human diet and bone collagen – different ratios in the kinds of plants we eat and different ratios between terrestrial and marine foods. 13C is more abundant in certain kinds of tropical plants, such as corn, and in the oceans. Carbon isotopes can tell us about the types of plants we eat and the importance of seafood in the diet. Thus, less negative values for collagen in bone mean either marine foods or C4 plants in the diet, or both. Nitrogen isotopes are used in much the same way as carbon isotopes, but they provide different information about diet. The ratio of 15 N (0.37% of all nitrogen in nature) to 14 N (99.63% in nature) is used in pale diet studies. Nitrogen is reported as d15N and values in human bone range from approximately –5‰ to +10‰. This nitrogen ratio is measured in bone collagen using a mass spectrometer. Nitrogen isotopes can tell us about the importance of meat in the diet, the role of freshwater fish, and the tropic level of human diets. Thus, a more positive nitrogen isotope ratio reflects a higher tropic level (Price and Burton 2011: 92-94).

Strontium Isotopes

Strontium isotopes, reported as the ratio 87Sr/86Sr, have been used primarily in the study of human movement in the past. There are, however, a number of other potential applications usually involving the sourcing or proveniencing of other kinds of objects and materials such as pottery, stone, textiles, or animals. The analysis proceeds through the sampling of tooth enamel to obtain the isotopic signal of the place of birth. The local isotopic signal can be determined in several ways: in human bone from the individuals whose teeth are analyzed, from the bones of humans or archaeological fauna at the site, or from modern fauna in the vicinity. The local geological isotope signals of strontium have been constant over the last several 1,000 years. These isotope ratios have been reported for the rocks, soils, and waters of the region of human and faunal remains from archaeological contexts throughout the region. Dental enamel, especially in teeth less than a few millennia old, is relatively robust against digenetic alteration. The permanent first molar is preferred both for consistency and the fact that the enamel of this tooth forms during gestation and very early childhood. Preparation involves lightly abrading the surface of a single cusp of a molar using a dental drill to remove surficial dirt and calculus and also the outermost enamel due to the possibility of contamination by diffusion. This cusp is then cut from the tooth with a crosscut blade and any remaining dentine removed with a drill. If a clean cusp is not available, a small chip is removed from the side of the molar or 5–10 mg of powder is drilled from the enamel. Samples weighing 2–5 mg are then dissolved in 5-molar nitric acid. The strontium fraction is purified using ion-specific resin and eluted with nitric acid followed by water. This solution is loaded onto a titanium filament for placement in the instrument. Isotopic compositions are obtained on the strontium fraction thermal ionization mass spectrometer (TIMS). This is a single focusing, magnetic sector instrument equipped with multiple Faraday collectors. Strontium is placed on a thin filament and measured. 87Sr/86Sr ratios are corrected for mass fractionation using an exponential mass fractionation law. 87Sr/86Sr ratios are reported relative to a value of 0.710250 for the NIST 987 standard (e.g., if the 87Sr/86Sr ratios for the standards analyzed with the samples average 0.710260, a value of 0.000010 is subtracted from the ratio for each sample). Strontium isotope analyses have been used successfully in a number of studies. The basic principle involves comparison of isotope ratios in human tooth enamel with local levels in bone or other materials. Because isotopic ratios vary geographically, values in human teeth (marking place of birth) that differ from the local ratio (place of death) indicate migration (Price and Burton 2011: 94-98).

Mass Spectrometers

Because mass spectrometers can resolve atomic weights that differ by less than one atomic mass unit (AMU), they are able to measure isotope ratios for a specific element. Many elements have atoms of more than one atomic weight. Although they are chemically identical, isotopes of the same element have a different number of neutrons – which change the weight but not the chemical properties – in the atomic nucleus. For example, all strontium atoms have 37 protons, which define strontium as a chemical element. Stable strontium atoms can have 47, 49, 50, or 51 neutrons yielding atomic weights (neutrons plus protons) of 84, 86, 87, and 88, respectively. Importantly, one of these, 87Sr, is radiogenic, created by the decay of 87Rb, which has a half-life on the order of 50 billion years. The ratio of 87Sr (7% in nature) to86Sr (10% in nature) varies and has significant archaeological applications. Mass spectrometers (aka, mass specs) do not use visible light or other wavelengths in the electromagnetic spectrum. These instruments do, however, separate atoms and molecules into a "mass spectrum" according to their weight. They then count the number of particles at a known weight that corresponds to a specific element or molecule. Mass specs sort particles according to their weight by putting an electric charge on the particle and accelerating the particle through an electric or magnetic field (or both).There are several different types of mass spectrometers. One common type is the quadrupole mass spectrometer in which atoms with an electric charge are accelerated inside of four metal rods to which alternating voltages are applied. If the frequency of the voltage change is just right, then an atom of the desired weight is attracted from one rod to the next as it passes among the rods toward the detector. A lighter atom will be more quickly drawn to one of the electrified rods and expelled; a heavier atom will be too sluggish to respond to the alternating voltage changes. Thus, at a particular voltage and frequency of change, only atoms of a specific mass can successfully traverse the quadrupole device toward the detector; heavier and lighter atoms are thrown out. Quadrupole mass spectrometers have relatively low resolution and have some problems with interferences. Two elements with the same atomic weight, e.g., CaO+1 and Fe+1, both with a mass of 56, cannot be distinguished. Better resolution of masses and alleviation of the problems with interference can be obtained by using a strong magnet. “Magnetic sector” mass specs accelerate ions into a strong magnetic field, which applies a force pushing the atoms in a direction perpendicular to the line of their movement. The magnetic field pushes lower weight particles to the side more easily than heavy ones, so that the lighter particles are deflected more from their original path. A simple analogy for this mechanism would-be a fan blowing perpendicular to a moving stream of golf balls and ping-pong balls. The ping-pong balls will be deflected further from their course than the golf balls. By adjusting the magnetic field, like adjusting the speed of the fan, the deflection can be precisely calibrated so that a particular mass arrives at the detector, while others of different weight are deflected short or wide of the detector and not counted. Thus by putting a particle detector at an angle to the original flight path of the atoms, one can focus a particular mass range on the detector by choosing an appropriate magnetic field strength. The strength of the magnetic push is proportional to the speed of the particle, so that varying the electric field that accelerates the particles adds a further degree of control over mass selection. These instruments are generally much larger (and more complicated and costly) than quadrupole instruments. At the same time, magnetic sector mass specs can resolve differences in mass much less than one AMU and can eliminate much of the interference between molecules and atoms with the same weight. Magnetic sector instruments are further distinguished by their method of sample introduction – how the sample is put into the electromagnetic field. Many instruments today use plasma, identical to that in optical ICP spectroscopy (ICP-MS).In the mass spec, the plasma is used to ionize the atoms. Although the plasma emits the characteristic spectra used in ICP-OES, this visible light output is not used by the mass spectrometer. Neither quadrupole nor magnetic sector machines with just a single ion detector, known as a "collector," have adequate precision (better than 0.01%) for most isotope ratio studies. For isotope ratios, multiple collectors are used so that measurements of the different isotopes can be done at the same time. Multiple collectors are commonly employed with the ICP-MS discussed above ("MC-ICP-MS") and on thermal ionization magnetic sector mass spectrometers (TIMS). TIMS uses a wire filament on which the purified element of interest is heated to ionize the sample ("thermal ionization"), instead of using plasma.ICP instruments are designed for input of aqueous solutions, but many archaeological samples such as lithics and ceramics are not easily put into solution. Thus a laser is sometimes used on the front-end of the ICP-MS ("laser ablation," or LA-ICP-MS). The laser is focused upon a small spot on the sample and ablates small part of the material into a gas stream that flows into the plasma. Mass spectrometers usually measure two or more isotopes at one time and calculate their ratio. Standards are measured at the same time in order to confirm the precision of the instrument and allow corrections to be made if needed. The results of the analysis provide the ratio measurements along with several other kinds of information (Price and Burton 2011: 98-102).

Organic Analysis

The foods and many of the raw materials that humans use are organic – meat, fish, fowl, vegetables, fruits, wood, hide, bone, antler, thatch, fur, and more – and come from living things. These materials were once abundant at the living places of prehistoric people. The bad thing is that in most cases this "biological" component of the past is very susceptible to decomposition and degradation and normally does not survive to the present. Fungi and bacteria feed on carbon-based materials and eventually consume them. The good news, however, is that those biological materials sometimes leave traces in and on artefacts and sediments that can survive for thousands of years. A variety of archaeological materials may contain trace organic compounds, including ceramics, stone tools, grinding stones, cooking slabs, plaster, fecal material, soil, and sediments. The best preservation seems to be in artefacts such as pottery that have absorbed trace organic compounds into their structural matrix, reducing the accumulation of "contaminants" from diagenesis, handling, and post depositional treatments, as well as the oxygen-induced degradation that can interfere with the identification of the original parent material. These organic molecules appear to bond to clay and to cling tightly to that bond over long periods of time. Organic compounds from the interior of ancient potsherds, for example, have been dated to more than 6,000 years before present. Trace organic compounds are distinguished from visible organic residues such as overcooked food on pottery or other macroscopic organic remains. Analysis of trace organic compounds, which have adhered to or been absorbed into the structural matrix of archaeological materials, can provide information about past artefact function, diet, and other aspects of prehistoric societies. This branch of archaeometric is sometimes referred to as molecular or "bimolecular" archaeology. Common organic residues in archaeology include lipids, amino acids, nucleic acids, simple sugars, terrenes, and hydrocarbons. Lipids are a major component of such organic residues and the component most studied by archaeological chemists. Lipids are a generic category of compounds that originate as constituents of living tissues defined by (1) their insolubility in water (hydrophobic), (2) solubility in organic solvents such as chloroform, methanol, or ether, and (3) they contain long-chain hydrocarbon groups in their molecules. Lipids are the most efficient energy storage molecules in cells. Although the term lipid is sometimes used as a synonym for fats, fats are a subgroup of lipids. There are many different forms of lipids, including alcohols, aldehydes, fatty acids, waxes, bile acids, and sterols. Of these, the most relevant in archaeological studies are the fatty acids and sterols. Their identification in archaeological contexts provides a means of distinguishing the biological materials that were originally present. Fatty acids, the building blocks of storage fats, are long-chain hydrocarbons with a terminal carboxylic acid group (–COOH). Fatty acids in which all the other carbon atoms are bonded by single bonds to four other atoms of carbon or hydrogen are known as "saturated" fatty acids because they have the maximum amount of hydrogen. Many important fatty acids have carbons that are doubly bonded to each other, reducing the total amount of hydrogen by two atoms for each double-bond. These are thus known as unsaturated fatty acids. Those with just one carbon double-bond are known as monounsaturated and those with more than one are known as polyunsaturated fatty acids. Fatty acids are identified in a shorthand notation by the number of carbon atoms in the hydrocarbon chain followed by the number of double bonds. Fatty acids are found in free form only in small quantities; in most cells they are combined with the alcohol glycerol to form glycerides. Glycerol can combine with one, two, or three fatty acids to create monoglycerols, diclycerols, and triglycerols, respectively. Lipids tend to survive better than other organic compounds in archaeological contexts and are amenable to sensitive methods of analysis such as gas chromatography/mass spectrometry

(GC/MS). Their insolubility in water increases their chances for survival. Lipids have been recovered from sediments that are millions of years old and have been identified in materials where no cellular structure remains. Lipids are also important because of their specificity. Certain kinds of lipids differ greatly not only between plants and animals, but among the various families and genera of plants and animals. Also, because fatty acids in animals tend to be mostly saturated fatty acids and polyunsaturated fatty acids are known mainly in vegetable oils, there is an enormous difference between plants and animals in the ratio of polyunsaturated to saturated fatty acids. Thus, an analysis of this ratio can give some indication of vessel use. Diagnostic fatty acids tend to be unsaturated, i.e., with one or more carbon double bonds, which are also those most susceptible to decomposition. In as little as 6 months, unsaturated fatty acids can degrade to the point that no diagnostic markers remain and the ratio of unsaturated acids (suggesting plants or fish) to saturated acids (suggesting other animal fats) changes too significantly to use simple unsaturated to saturated fatty acid ratios as reliable dietary indicators. Although the major stress in archaeological research has been on fatty acids, sterols may also be useful because of their potential to further resolve the identification of organic traces. There are substantial differences among the plants and animals. Sterols are widely distributed in animals (zoosterols) and plants (phytosterols) and they can strongly discriminate different plant and animal classes, possibly to species levels. There are no major, and extremely few minor, sterols that are present in both plants and animals. This means that if several parent materials were stored in a vessel or processed by an artefact, division of the residues into plant and animal groups should be straight forward, and the chemical signature of the sample can be more readily identified as to its parent material. There are a number of lipid compounds specific to fecal material, including sterols, bile, and some others that can be found either in soils or coprolites. A byproduct of these sterols is a compound known as 5b-stanol, produced in the gut of animals from cholesterol. 5b-stanol is a distinctive marker in animal feces. The presence of this compound in prehistoric agricultural fields has been used as evidence of intentional fertilization. Investigations of sterols in archaeological contexts have generally been limited to the study of coprolites or preserved human tissue although some applications to ceramics and sediments have been reported. Although most of the organic residues have involved lipids, some have studied protein residues and others have looked for remains of sugars and complex carbohydrates. Proteins are complex, sometimes immensely complex, molecules made of long chains of amino acids connected through a series of peptide bonds. An amino acid is an organic molecule that has a carbon characterized by bonds to four distinct functional groups: a carbonic acid group, an amino group, hydrogen, and the remainder of the organic group "R" by which the amino acid is identified. A peptide bond forms when the amino group of one amino acid reacts with the carbonic acid group of another, with the release of water. Proteins normally have long chains of peptides with thousands and thousands of peptide bonds. Even though proteins have problems of degradation and preservation and have-not received the attention that lipids have, there is a great deal of current excitement about protein analysis because of the tremendous potential for proteins being highly source specific. Moreover, not only do they vary by species, but humans and other animals have highly evolved immunological responses by which species specific proteins are recognized. These immunological responses are now being employed in the laboratory with similar specificity to identify small traces of proteins from individual species. For example, trace blood residues on a stone tool can be tested specifically for immune or "anti-antibody" responses for trout, deer, bear, and other individual species. Nonetheless even the analysts themselves caution that the research is relatively new and must be critically evaluated. Most of the effort, and success, in the organic analysis of archaeological residues has been in characterizing specific organic molecules and relative abundances of fatty acids retained in potsherds. Unglazed pottery absorbs food residues as can been seen in the dark stains that accumulate in new pottery. These residues can be extracted from their ceramic matrices with common organic solvents and identified by their diagnostic spectra with the use of liquid chromatography or gas chromatography coupled with mass spectrometry (LC–MS and GC–MS, respectively).Initial investigations of lipids in archaeological materials relied on thin-layer chromatography (TLC) or IR spectroscopy. These techniques provided only broad classifications of the organic compounds under investigation and were not well suited for the analysis of degraded substances. The use of a GC/MS instrument has become standard practice in the analysis of organic compounds. GC/MS not only separates different organic compounds but also measures their mass spectra, which make possible both a positive identification of each component and a sensitive way to determine minor variations between similar components. These variations include differences in the carbon chain structure, changes in the position of double or triple bonds, and alterations in the direction of branch chains, all of which can be diagnostic of parent material. No doubt as scientific instrumentation becomes more sensitive to the identification of ancient compounds and as these instruments become more accessible to archaeology, studies of trace organic compounds with become a more important aspect of archaeometric. Although the analysis of trace organic compounds has a great potential in archaeological research, a number of problems remain, largely due to post depositional changes in the molecules either through contamination – the addition of new materials to the matrix – or the breakdown of the original molecules into small, unidentifiable components. Another factor complicating the identification of parent materials is the processing or storage of multiple parent materials within the same ceramic vessel. Since different plants and animals have different kinds and percentages of lipids, the mixing of several different species will alter the "signature" pattern making it difficult to distinguish the individual parent materials responsible for the residues. Basic procedures for the analysis of organic residues involve extraction of the molecules by (1) Powdering the archaeological material, (2) Ultrasonicating the powder in a mixture of chloroform and methanol, (3) Centrifuging and decanting the total lipid extract (TLE), (4) Decant dried in a stream of nitrogen. (5) TLE is then reacted with a compound to produce a more volatile set of derivative compounds. These volatile derivatives are then introduced into a Gas Chromatograph/Mass Spectrometer (GC/MS). The GC/MS separates of the different molecules by passage through a long column containing a solid that slows some of the gas molecules more than others by physical and chemical interactions. As the column is heated the most volatile compounds pass more quickly through the column with the least volatile appearing last. The molecules exit from the tube sequentially, in order of decreasing volatility, and pass over a detector (e.g., a flame) that registers a peak for each type of molecule. These molecular components are individually fragmented in the detector and injected into a mass spectrometer that sorts the fragments by their mass. Because different molecules break down in characteristic ways, analysis of these mass fragments provides additional information about the identity of the original molecule. These mass spectra are then compared with the spectra from known molecules in order to make identifications. Technology has now advanced to the point that one can obtain stable d13C andd18O ratios of individual fatty acids. Because different species isotopic ally fractionate fatty acids in different ways and to different degrees, these ratios can be used to identify further the fats from different sources. One such study examined the use of ceramic containers as oil lamps and characterized the type of oil used on the basis of fatty acids from pigs, cattle, and sheep. Dairy products have been identified in Neolithic ceramics through the same methods (Price and Burton 2011: 102-109).

Methods of Organic Analysis

Two general approaches have been taken in the analysis of organic materials. The first involves the separation of the complex mix of organic molecules by chromatography; each component is then identified by MS. Often this involves the search for a few, highly diagnostic molecules. The second approach, less frequently employed, involves the bulk analysis of organic compounds by Nuclear Magnetic Resonance (NMR) or IR spectroscopy that measures the atoms and bonds involved in the molecules. The spectra of residues can provide a fingerprint of the remaining material, depending on conditions of preservation and the extent of contamination. Initial investigations of lipids in archaeological materials relied on TLC or IR spectroscopy. These techniques provided only broad classifications of the organic compounds under investigation and were not well suited for the analysis of degraded substances. The use of a GC/MS instrument has become standard practice in the analysis of organic compounds. GC/MS not only separates different organic compounds but also measures their mass spectra, which make possible both a positive identification of each component and a sensitive way to determine minor variations between similar components. These variations include differences in the carbon chain structure, changes in the position of double or triple bonds, and alterations in the direction of branch chains, all of which can be very diagnostic of parent material. Basic procedures for the analysis of organic residues involve extraction of the molecules by (1) Powdering the archaeological material, (2) Ultrasonicating the powder in a mixture of chloroform and methanol, (3) Centrifuging and decanting the TLE, (4) Which is then dried in a stream of nitrogen, and (5) The TLE is then introduced into a GC/MS. The GC/MS separates the hundreds of molecules by passage through a long column containing a solid that slows some of the gas molecules more than others by physical and chemical interactions. The molecules then exit from the tube sequentially and pass over a detector that registers a peak for each type of molecule. The GC/MS produces a chromatograph, a spectrum of the weight and amount of the various molecules present in the extract. These spectra are compared with known materials in order to make identifications (Price and Burton 2011: 109).

Chromatography

Archaeological residues are often a complex mixture of original molecules, degradation products, contamination from the burial matrix and finds processing, storage, etc. Further separation of the mixture, combined with identification of the components, is required. Chromatography is used to separate mixtures into their molecular components, although chromatography may be used for the separation of inorganic compounds and their different species. The ''classical'' techniques of column chromatography and thin layer chromatography (TLC) are not primarily used as analytical tools in their own right, but often as preparative methods for more detailed analysis. The principles of gas chromatography (GC) and high performance liquid chromatography (HPLC) are very important for an archaeologist (Pollard et al. 2007: 137).

Technique	Stationary phase	Mobile phase
Thin layer chromatography (TLC)	Solid (silica gel)	Liquid (solvent, often a mixture). Also called developer.
Classical column chromatography	Solid (silica gel)	Liquid (solvent, often a mixture). Also called eluent.
Gas chromatography (GC)	Bound liquid in matrix	Gas (H2 or He).
High performance liquid chromatography (HPLC)	Bound liquid in matrix	Liquid (solvent, often a mixture).

Table No. 8. Definition of the four main chromatographic techniques with a description of the associated stationary and mobile phases (Pollard et al. 2007: 138)

Gas/Liquid Chromatography–Mass Spectrometry

In the laboratory, the most common instrument for the study of organic remains combines the techniques of chromatography and MS to separate different molecules and identify them, respectively. The normal techniques used to separate mixtures of different organic substances for identification are called "chromatographic" methods. Chromatograph literally means "colour writing" and early methods produced a colored graph showing the separation of components in a sample. The basic principle underlying these methods can easily be demonstrated by creating an ink spot on a piece of absorbent paper and then adding a few drops of alcohol. As the alcohol spreads across the paper, different components in the ink will move outward from the spot at different speeds depending upon their solubility in alcohol. The result will be a set of approximately concentric rings each ring holds a different component of the ink (commonly a different colour). Chromatographic methods involve a "stationary phase," in this case the paper, and a "mobile phase," in this case the solvent used to separate various components of a sample. The separation of the sample compound is based on a physical property that effects among the separate components of the compound differently. In our ink example, solubility is the property that separated the components. Paper chromatography is in fact one of the early methods for the analysis of organic compounds. This technique uses paper as the stationary phase and a solvent such as alcohol as the mobile phase. Usually the samples are arranged along the bottom edge of a sheet of absorbent paper, which is placed in a tray with as hallow layer of the solvent. More commonly, the sheet of paper is replaced by sheet of glass coated with a thin layer of an absorbent material such as silica gel. In this method, known as "TLC," the various components move various distances up the glass sheet depending on their relative solubility in the solvent. The sample components are rarely as colourful as in the ink example. However, the sheet can be sprayed with a reagent that will react with specific components to produce a colour band, or the components, which are usually organic, can be chemically or physically burned to produce a charred stain where an otherwise invisible component is located. Fluorescent gels can be used in conjunction with a UV lamp to reveal the locations of many components without using chemical reagents or charring. While chromatographic methods separate chemical compounds, they do not identify them as specific compounds. For this purpose one needs a good knowledge of what is most likely to be in the mixture. Known substances can be analysed alongside the unknown samples. TLC and paper chromatography, while quite simple and inexpensive, are limited in their application to relatively simple mixtures. Advance instrumental methods have been developed that allow smaller samples to be analysed with much better resolution of different compounds. These methods also use the same principal of using stationary and mobile phases based upon a specific physical property that isolates the components of the mixture. The most widely used methods are distinguished by the mobile phase, whether a liquid solvent (LC) to separate materials by solubility or a heated gas (GC) to separate materials by their volatilities. Other chromatographic methods use refined stationary phases, such as microscopically porous materials that act like filters. These filters allow tiny molecules to pass, but larger molecules cannot. These methods are generally used to separate mixtures of quite large organic molecules such as fatty acids, oils, and waxes. Instrumental methods differ from paper and TLC in that the sample components are separated by time, rather than distance. Instead of measuring the distance that substances move along a plate, the time at which the materials move past a specified point in space is recorded. More mobile (e.g., more soluble or volatile) substances arrive earlier. The relative abundance of each component can usually be determined as well. These instrumental methods also have limitations in that they do not provide specific identification of the components they record. For relatively common mixtures with known components, reference substances can be run through the instrument and results compared to the unknowns. Because archaeological materials are old and organic components have decomposed over time, there is a need to identify broad array of complex mixtures and their often-incomplete contents. In order to get more detailed information, instrumental chromatographs are connected to mass spectrometers. The compounds separated by chromatography are sent into the mass spec as they arrive, so that the output of the chromatograph is the input of the mass spectrometer (thus the synonyms "GC–MS" and "LC–MS"). The mass spectrometer calculates the mass and abundance of the unidentified component and this information can be used to identify the material. In addition, molecules of a sample commonly break apart in characteristic ways at the chromatograph/mass spectrometer interface. The mass spec measures the masses and relative abundances of these distinctive sub molecular fragments as well. A knowledgeable analysis of these fragmentation patterns, along with computerized comparison to large databases of such fragmentation patterns, helps to identify unique molecular compounds (Price and Burton 2011: 109-113).

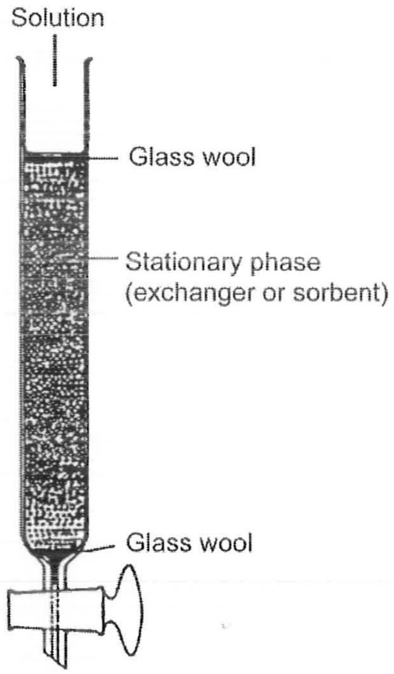

Figure 8: Diagram of classical liquid column chromatography. The sample is introduced at the top of the column, and the different components travel downwards and are separated. They can be collected in sequence from the tap at the bottom (Pollard et al. 2007: 140).

Mineral and Inorganic Compounds

Minerals are inorganic compounds that are found in nature and have both a well-defined composition and crystalline arrangement of atoms. Coal and petroleum hydrocarbons are organic and thus not minerals. Obsidian is not a mineral because it has neither crystalline structure nor a specific composition. Stones such as chertand flint, which are mainly silica, SiO2, have a relatively precise composition but lack crystalline structure, so are not minerals. While copper is a mineral, brass and bronze do not occur in nature and do not have a fixed elemental composition, so they are not minerals. A synthetic material can be a mineral, however, as long as it is also found in nature. Hematite can be produced artificially by firing ceramics in an oxidizing environment, but it is still considered mineral because hematite can be found in nature. A synthetic ruby is likewise a mineral because rubies do occur in nature, but modern cubic zirconium is not. Because minerals are defined both by composition and structure, minerals can have the same composition but different structures and thus are distinctly different minerals. Diamond and graphite are both pure carbon but have different atomic arrangements and thus are different materials, with quite different properties. Likewise calcium carbonate, CaCO3, has a definite composition but this is not mineral name because calcium carbonate can occur as aragonite or as calcite, each with a unique arrangement of atoms. Because this structural arrangement of atoms is essential to the identity of an element, methods used to study minerals differ from those used to assess elemental composition. The major tools include microscopy, X-ray methods, and molecular spectroscopy. These directly examine the molecular structure and the kinds of bonds between atoms rather than elemental abundances. Because rocks are composed of one or more minerals, if these cannot be determined visually in a hand-sample, they are examined with the petrographic microscope or, in the case of opaque oxides, ore minerals, and metals, with the metallographic microscope. Because rocks are identified compositionally, it's sometimes necessary to assess the percentages of the different minerals, which can be done by using a grid in the field of view of the microscope and counting the number of grains of each mineral at the cross-sections of the grid. For example, a 10 × 10 grid has a hundred intersections. If 40 of these intersections fall on a quartz grain, then approximately 40% of the rock is quartz. By taking several such counts of the grains, one can accurately assess the mineral components and identify the rock. Because minerals have well-defined elemental compositions, one can assess the major elemental composition of a rock from this quantitative measurement of mineral abundances. Just as major elements are used to identify materials, while trace elements are used to "fingerprint" the origins of materials, the determination of major minerals is mainly used to identify rocks and minerals, e.g., fine-grained pyroxene, plagioclase, and olivine imply that the rock is basalt, while rare trace-minerals can be used to "fingerprint" the origins of geological materials. Tools such as XRD and IR spectroscopy are useful when the rock contains only one or two minerals, but both IR and XRD spectra become too complex, with multiple overlapping peaks, when there are more than a few minerals. Thus these tools are mainly used for identifying the major mineral components. When there are more than a few minerals, e.g., for most rocks, the petrographic microscope is the most useful too, The SEM using backscattered electron imaging coupled to an X-ray detector is also a powerful tool in identifying the compositions of individual minerals in a rock section, although it is more difficult with the SEM to quantitatively determine the percentage of each mineral because of the limited field of view at such high magnification. It is invaluable, however, in being able to determine the identity of minerals smaller than 10 or 20 mm, which can in turn be valuable for provenience studies of geological materials including ceramics (Price and Burton 2011: 115-116).

Petrography

Optical mineralogy employs the use of polarized light, which is light waves in which all the waves are oriented in the same direction, to probe the structure of inorganic materials. For materials that are homogenous without crystalline structure such as obsidian, there is no preferred orientation that would preferentially affect light polarized in any particular direction. Likewise, for highly symmetric minerals such as halite, the mineral name for sodium chloride, and diamond, which have cubic crystals, there is no preferred orientation within the crystal and no effect on polarized light. Most minerals, however, lack such symmetry and refract light differently in different directions. By using the directional properties of polarized light and orienting the minerals in different directions with respect to the direction of polarization, one can determine the nature of the crystal symmetry of a mineral. This information along with other optically observable features such as colour and cleavage – the way in which a crystal breaks – usually suffices to uniquely identify mineral. A petrographic microscope is a special kind of binocular microscope, designed for the study of thin sections – slices of rock, pottery, or other materials –ground and polished to a thickness of only 0.3 mm. This slice, or section, is so thin that light from beneath can pass through the material. Two kinds of light are used for viewing thin sections, normal and polarized light. Normal light is the standard source from the microscope. Polarized light is constrained to a single plane, in the same way that polarized sunglasses reduce glare. Many minerals change colour and brightness when polarized light passes through them. These changes are a useful way to identify specific minerals in a thin section. While the petrographic microscope was designed by geologists to examine the minerals within rocks, archaeologists mainly use instrument this to identify the mineral grains in sand-tempered pottery, as well as to record grain-size and textural attributes that can be useful in determining the provenience of the pottery. It uses similar optics and polarized light to study metals and metal ores, except these are opaque when viewed in a thin section, so the metallographic microscope uses reflected light rather than light transmitted through the sample asin the petrographic scope. Because samples are not transparent, they don't need to be sliced to the precise 0.03 mm required by thin sections. Instead samples are usually embedded in a small resin plug with a flat surface that is then highly polished, ideally removing surface imperfections down to approximately a micron. This allows one to see the grain structure of metals, which can be highly informative about technology. The metallographic microscope is used primarily for studying technological evolution from the use of native metals through the development of bronze and iron to recent historical metallurgy. When copper is shaped by hammering at low temperatures, processes known as "work-hardening," the copper grains become flattened, long, and thin. While copper atoms move easily within individual grains, they are blocked by the boundaries of grains and can't move easily or far within the thin grains of work-hardened copper. Thus work-hardened copper cannot be as easily deformed or shaped as copper that has not been worked. This makes it stronger and harder but also more brittle. One can, however, restore ductility to copper by heating it, which allows the grains to recrystallize into much larger, more equidimensional grains, in a process known as "annealing" (Price and Burton 2011: 115-118).

X-Ray Diffraction

In 1913, shortly after the discovery of X-rays at the turn of the century, William Henry Bragg and his son, William Lawrence Bragg examined patterns made by-rays as they passed through various types of crystals such as halite. They not only correctly surmised that the patterns were a response to the regular arrangements of atoms within the crystals, but also developed the rigorous mathematics from which one could determine the arrangements of atoms from the X-ray patterns. For this they were awarded the Noble Prize, making William Lawrence Bragg at age 25 the youngest recipient ever.XRD works a bit like that irritating flash of sunlight from the flat face of your wristwatch that aligns perfectly to hit you in the eye (Price and Burton 2011: 119-120).

IR Spectroscopy

Extending beyond the visible region into the longer, lower energy wavelengths of the electromagnetic spectrum, we enter the IR and microwave regions. These wavelengths, on the order of fractions of a millimetre up to centimetres, are too large to interact with individual atoms. This scale is appropriate, however, for groups of atoms such as molecules. IR spectroscopy works by inducing vibrations within molecule. Specific IR wavelengths correspond to particular modes of vibrations among particular atoms. For example, molecules of carbon dioxide (CO2) can absorb photons with a specific energy by transforming this energy into vibrations that stretch the carbon–oxygen distance; photons of a different energy cause vibrations in a mode that bends the molecule along its oxygen–carbon–oxygen axis. Water has similar vibration modes, but the specific atoms are different so the wavelengths at which it absorbs light are different from those of CO2, even though the types of vibrations are similar. In the most basic form, IR spectroscopy is similar to colorimetric and absorption spectroscopy. The spectrometer projects IR light through a transparent film of the unknown sample and the amount of light absorbed by the sample is recorded over the relevant wavelengths. Many modern instruments, however, use "Raman scattering, "which is similar to a fluorescent or emission technique. In Raman-IR, a particular wavelength is projected onto a sample and the wavelengths of the light scattered at high angle are recorded. Rotations of the molecules as well as vibrations can absorb energy from the incident light so that the scattered light will be missing this energy.

Because decreasing energy corresponds to increasing wavelength, the wavelength of this scattered light will increase by a precise amount corresponding to the energy loss of the vibrations. Changes induced by the incident light can also produce vibration and rotational modes with less energy and the scattered light can thus also be shifted to lower wavelengths of correspondingly higher energy. The resulting spectra are often more characteristic of materials than are simple IR spectra. The Raman method can be applied to a much wider array of materials than standard IR spectroscopy. Because it only examines light reflecting off the surface of an object, the method is non-destructive. Portable instruments for Raman IR spectroscopy are available that allow the method to be used in the field and in museums (Price and Burton 2011: 120-122).

CHAPTER 2

Scanning Electron Microscopy of the Archaeological Material of District Shangla, Pakistan

The chapter is divided into three parts. The first part is about the research conducted at District Shangla. The second part is an introduction to scanning electron microscopy and the third part is about the scanning electron microscopy of the archaeological material acquired from the District Shangla.

Part 1

The research has been conducted for the archaeological survey of District Shangla since July 2012 and sites have been documented from both the tehsils of District Shangla. Following is the description of some selected Buddhist sites tehsil wise (Unpublished report of Dr. Ghani-ur-Rahman).

PURAN TEHSIL

Purim is bounded on the west by Swat district, on the north by Alpurai tehsil of Shangla, on the south by Buner and on east by Mansehra. Tehsil Puran is subdivided into Puran, Martung and Chakesar. Puran Valley then is subdivided into Babuzais and Makhuzais. While Babuzais cover the area from Yakhtangi to Aloch the Makhuzais are between Aloch and different smaller valleys towards dwasaroghar.

The site has been visited twice each time for a week and about 70 sites including Buddhist and Muslim period remains have been documented. The Buddhist period remains include Settlement sites, Monastery remains and rock carvings. While the Muslim period sites are 200 or 300 years old graveyards and mosques.

Objectives:

The objectives of the survey are:

- To document the so far unrecorded archaeological sites and historical monuments in Puran
- To document their present state of preservation.
- To recommend their future preservation measures.
- To train the archaeology students of the TIAC.
- To make the locals aware of the importance of their cultural heritage.

A short description of the selected sites and monuments of Puran is enumerated in the following section.

Ocha Dara, Braim village

A Buddhist site in Ocha Dara, Braim is situated 22 km N-W of Chawgah. The site is approx. 100 m long and 60 m wide. Stone wall structures are visible. Pottery fragments were collected from the site. Presently the site is a cultivated land.

Garhai Sar, Braim Village

The site is the remains of a probable fortified Buddhist Monastery located on a hill top in UC Ismail Khel. The site is about 600 m long and 300 m wide. Stone structures and potsherds were recorded.

Garhai Gumbat

Garahi Gumbat is a Buddhist site which can be assumed by seeing the wall structures and collected potsherds. As the name indicates here there was a stupa which is called gumbat by the locals. The site is presently a cultivated land and no more a gumbat (stupa) exists.

Sanda Sare (Swati)

A settlement site, probably, of the Buddhist period was documented in Sanda Sare, UC Aloch, half a km s-w of Aloch. The other nearest village is Nimkale. It is on the right side of the Aloch-Chawga Road. This site is a very large site and is about 500 X 300m. A wall structure can be seen of the Buddhist period. Pottery pieces were collected from the site in abundance. Bones were also found. It seems a settlement site of the Buddhist period.

Buwagai Chawgah

(Tarserai Chawgah)

A Buddhist site was recorded in Buwagai, Chawgah which has been destroyed. Only a wall structure can be seen. Potsherds and Iron nails were recorded.

Budrial, Dherai

In the Budrial area of Dherai, UC bar Puran are traces of a Buddhist period settlement. Another nearest village is Sanila. Wall structure was noted and potsherds collected in small quantity. Owner of the now cultivated field mentioned that he had found even complete pots in the filed.

Malango Sar, Agher Dara, Enawar

A Buddhist period monastery remains were documented on Malango Sar, Agher Dara, Enawar, UC Musakhel flanked on one side by dwasaro and on the other by Pandoria village. The site has been illegally excavated by antique hunters. The site is of about 40 X40 m dimensions. Destroyed wall structures were noted while almost no pottery pieces were found.

Shere pate, Agherdara, Enawar

Shere pate seems to be a Buddhist period settlement site at the foot of the Malangosar. Wall structures were noted and potsherds collected from the site which is a cultivated field now.

Kafiro Dherai Rock Carvings

Kafiro Dherai Rock Carvings locally known as Doma Domai were previously reported by Luca M. Olivieriin 1994 and then by the Pakistani team including Dr. M. Farooq Swati, Naeem Bacha and Jehan Mulk. It is situated in UC Musakhel and on Shikaulai-Pandoria-Enawar road. A very beautiful and a relatively large scale site having a group of Budhisattvas and a seated Buddha. The carvings have been recently damaged. The treasure hunters have tried recently to take the Buddha carving out of the boulder by drilling. It is still there but it might soon perish if no measures of protection were taken. The owner of the land has promised that he will no more let it be destroyed. In the survey by Swati sb and his team have already been mentioned that the shelter III was already destroyed and it is now shelter II which is being destroyed.

Kafiro Dherai Remains

Besides the Rock carvings is a huge site of Monastery remains of a rare type. The extent and structural remains indicate that it was a fortified monastery like the one in Nangrial (Thanks to Luca) and another in Qalatir which was visited by me in 2007. The monastery of this kind is constructed according to the availability of space on the hill top. It is about 400 X 30m.

The author has previously visited a monastery (Qalatir Monastery) of almost the same extent in Kukarai village on the road from Said Sharif to Murghzar. Almost the same kind of Monastery is that of Kafiro Dherai and Garaisar (included in this survey) in Puran and Nangrial in Malam Jabba Valley that was indicated to me by Dr. Luca M. Olivieri. It seems as if these types of monasteries flourished in the late period of Buddhism when they faced Huns and then were living in the environment of the Hindu Shahis. As it was not a peaceful period for them they constructed fortified monasteries.

Khonano Dherai, Shikaulai

Khonano Dherai is the site having Buddhist remains. The Dherai is situated in Khonano, Shiakulai, and UC Musakhel. Another nearest village is Kamlai. It is very near to the previously discussed graveyard and mosque in Khonano. The remains are of small extent as per the space on the small hill top. This indicates to the remains of a very small fortified monastery of about 25 m X 20m. Remains of the wall structures of monastery and fortifying cells are visible. Potsherd was collected. It is 18 km from Aloch and then half a km walking track to the left of the road.

Kamlai Remains, Shikaulai

Kamlai site is in UC Musakhel and Main Shikaulai road leading to Gokan, Buner. It is a site having Buddhist period remains. Wall structures are visible. Potsherds were collected. It is about 200 X 30m.

Jabagai Dherai, Chawgah (Swati)

Jabagai Dherai is situated in UC Chawgah nearest village Chawgah on Chawgah-Machkandai Road. The remains indicate to a Buddhist Monastery and a stupa. It is about 60 X 30m. Exposed features are parts of stupabase. Wall structures present here and there showing a large extent of the Monastery. Potsherds were collected. It is about 8.6 km from Aloch. And 1.5 km from Chawgah.

Badar Jabagai, Chawgah

A Buddhist settlement remains very near to Jabagai Dherai. The extent is about 250 X 100m. It is now a cultivated land but the owner reported that there are foundations of houses. A big boulder can be seen on the site. A cave like space is also observed beside the boulder. The boulder gives an impression as if it has been used for inscription like the ones in Mansehra and Shahbaz Garhi. A large number of potsherds were collected. The site seems to be very important and needs excavation. The owner reported that coins have been found while ploughing in the past. What he indicated seemed that the coins were of Greek period. The site is on the walking distance from the previous site, Jabagai Dherai. The site is 8.6 km from Aloch.

Bunerwal Rock Carvings (Luca, Swati)

Bunerwal Rock Carvings are in UC Aloch near Kotke village. The boulder Measures 10 feet X 7feet. A Buddha figure in dhayana mudra and other defaced figures can be seen. Preservation and protection is needed.

Marin, Nimkale

Marin Nimkale site is situated in UC Aloch. A small road detaches on the left side rom Aloch-Chawgahroad. It is a Buddhist Site of about 300 X 200 m extent. It is a cultivated land. Potsherds were collected and wall structures reported. The site is completely disturbed. It seems to be a settlement site.

Garai Sar, Towa, Bar Puran (Swat)

Grai Sar is situated in UC Bar Puran on Dherai-Chakesar Road. Potsherds were collected. Stones of wall structures are scattered on the site. Beads were reported by the owner. Charcoal was collected. Iron ores are scattered on the site. Excavation is needed. It was illegally excavated. It is 15 km from Aloch and 3.3 km from Dherai village.

Part 2

Introduction to Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) permits the observation and characterization of heterogeneous organic and inorganic materials on a nanometer (nm) to micrometer (μm) scale. The popularity of the SEM stems from its capability of obtaining three-dimensional-like images of the surfaces of a very wide range of materials. SEM images are used in a wide variety of media from scientific journals to popular magazines to the movies. Although the major use of the SEM is to obtain topographic images in the magnification range 10-10,000 x, the SEM is much more versatile, as we shall now see. In the SEM, the area to be examined or the microvolume to be analyzed is irradiated with a finely focused electron beam, which may be swept in a raster across the surface of the specimen to form images or may be static to obtain an analysis at one position. The types of signals produced from the interaction of the electron beam with the sample include secondary electrons, backscattered electrons, characteristic x-rays, and other photons of various energies. These signals are obtained from specific emission volumes within the sample and can be used to examine many characteristics of the sample (surface topography, crystallography, composition, etc.). The imaging signals of greatest interest are the secondary and backscattered electrons because these vary primarily as a result of differences in surface topography. The secondary electron emission, confined to a very small volume near the beam impact area for certain choices of the beam energy, permits images to be obtained at a resolution approximating the size of the focused electron beam. The three-dimensional appearance of the images is due to the large depth of field of the scanning electron microscope as well as to the shadow relief effect of the secondary and backscattered electron contrast. In the SEM, characteristic x-rays are also emitted as a result of electron bombardment. The analysis of the characteristic x-radiation emitted from samples can yield both qualitative identification and quantitative elemental information from regions of a specimen nominally 1 µm in diameter and 1 µm in depth under normal operating conditions. The evolution of the SEM and the specific capabilities of modern commercial instruments are discussed below (Goldstein 2003: 1).

The scanning electron microscope is one of the most versatile instruments available for the examination and analysis of the micro structural characteristics of solid objects. A major reason for the SEM's usefulness is the high resolution which can be obtained when bulk objects are examined; instrumental resolution on the order of 1-5 nm (10-50Å) is now routinely quoted for commercial instruments (Goldstein et al. 2003: 2).

One of the most promising advances in the development of the SEM is the capability to determine the crystal structure and grain orientation of crystals on the surface of prepared specimens. This capability makes use of diffraction of the backscattered electrons emerging from the specimen surface and is known as electron backscattering diffraction (EBSD) (Goldstein et al. 2003: 10).

The scanning electron microscope can also be used to obtain compositional information using characteristic x-rays. The development of an instrument for obtaining localized chemical analysis of solid samples (called an electron probe microanalyzer, EPMA) occurred at the same time as the development of the SEM (Goldstein et al. 2003: 10).

The SEM and its Modes of Operation

Obtaining a low-magnification (<1000 x) image of a rough threedimensional object is remarkably easy with an SEM. To obtain all the information the SEM can provide, however, requires an understanding of the major modes of microscopy and the electron beam parameters that affect them. The researcher will discuss the following microscopy modes: resolution mode, high-current mode, depth-of-focus mode, and low-voltage mode the electron beam diameter at the specimen limits the image resolution, and the amount of electron current in the final probe determines the intensity of the secondary and backscattered electron and x-ray signals. Unfortunately, the smaller the electron probe, the lower is the probe current available and the poorer is the visibility of image features. The angle of the conical beam impinging on the specimen governs the range of heights on the specimen that will simultaneously be in focus. The accelerating voltage (kilovolts) of the beam deters mines how faithful the image will be in representing the actual surface of the specimen. The operator must control these beam parameters to achieve optimum results in each microscopy mode (Goldstein et al. 2003: 21).

Functions of the SEM Subsystems

The two major components of an SEM are electron column and the control console. The electron column consists of an electron gun and two or more electron lenses, which influence the paths of electrons travelling down an evacuated tube. The base of the column is usually taken up with vacuum pumps that produce a vacuum of about 10-4 Pa (about 10-G torr, or roughly one billionth of atmospheric pressure). The control console consists of a cathode ray tube (CRT) viewing screen and the knobs and computer keyboard that control the electron beam (Goldstein et al. 2003: 22).

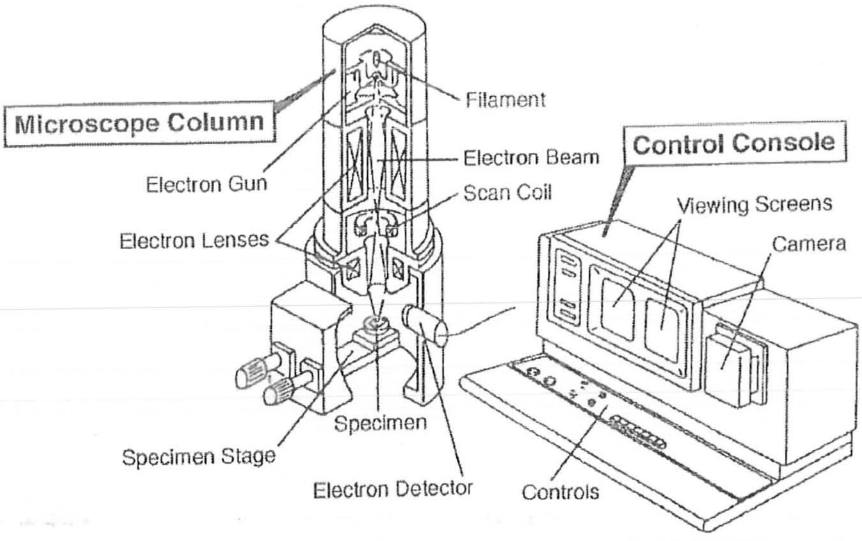

Figure 9: The two major parts of the SEM, the electron column and the electronics console (Goldstein et al. 2003: 22)

Electron Gun and Lenses Produce a Small Electron Beam

The electron gun generates electrons and accelerates them to energy in the range 0.1-30 keV (100-30,000 electron volts). The spot size hum a tungsten hairpin gun is too large to produce a sharp image unless electron lenses are used to demagnify it and place a much smaller focused electron spot on the specimen. Most SEMs can produce an electron beam at the specimen with a size of less than 10 nm (100Å) that contains sufficient probe current to form an acceptable image. The beam emerges from the final lens into the specimen chamber, where it interacts with the specimen to a depth of approximately 1µm and generates the signals used to form an image (Goldstein et al. 2003: 22).

Deflection System Controls Magnification

The scanned image is formed point by point. The deflection system causes the beam to move to a series of discrete locations along a line and then along another line below the first, and so on, until a rectangular 'raster' is generated on the specimen. Simultaneously, the same scan generator creates a similar raster on the viewing screen. Two pairs of electromagnetic deflection coils (scan coils) are used to sweep the beam across the specimen. The first pair of coils deflects the beam off the optical axis of the microscope and the second pair bends the beam back onto the axis at the pivot point of the scan. The magnification M of the image is the ratio of the length of the raster on the viewing screen to the corresponding length of the raster on the specimen (L). For example, a 100-μm wide raster on the specimen displayed on a 10-cm-wide viewing screen generates an image of 1000x magnification. When the operator requests an increase in image magnification, the scan coils are excited less strongly, so that the beam deflects across a smaller distance on the specimen. Note that the raster size on the specimen also depends on the working distance, the distance from the specimen to the bottom of the final lens. In a modern SEM the magnification is automatically compensated for each working distance to assure that the indicated magnification is correct (Goldstein et al. 2003: 22-24).

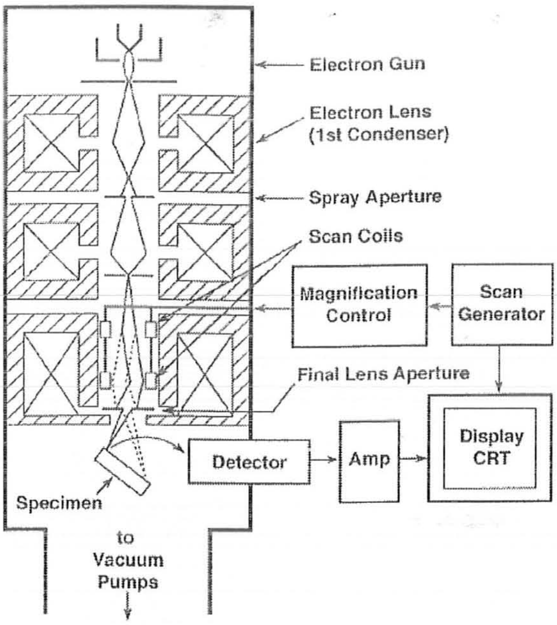

Figure 10: Schematic drawing of the electron column showing the electron gun, lenses, the deflection system, and the electron detector (Goldstein et al. 2003: 23)

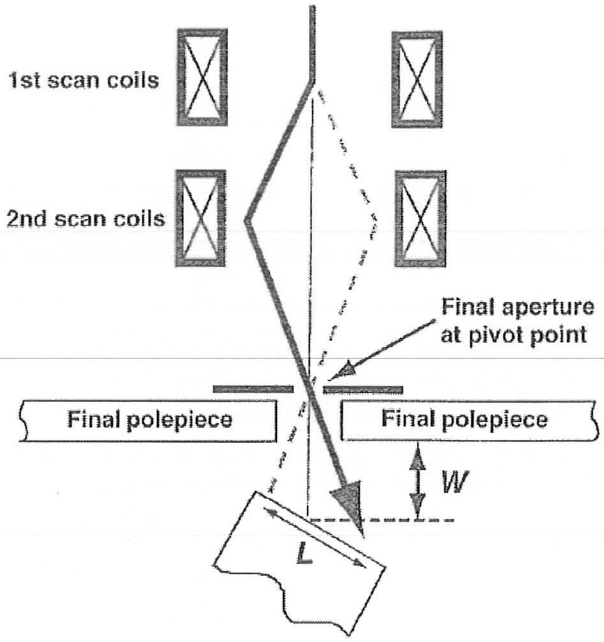

Figure 11: Deflection system inside the final lens. Working distance W is the distance between the specimen and the bottom of the final lens pole piece (Goldstein et al. 2003: 23)

Electron Detector Collects the Signal

Contrast in an image arises when the signal collected from the beamspecimen interaction varies from one location to another. When the electronbeam impinges on the specimen, many types of signal are generated and any of these can be displayed as an image. The electronics of the detector system converts the signals to point-by-point intensity that changes on the viewing screen and produces an image. The two signals most often used to produce SEM images are secondary electrons (SE) and backscattered electrons (BSE).The standard Everhart—Thornley (E—T) detector collects both secondary and backscattered electrons as shown in Fig. 2.4. Both SE and BSE signals are collected when a positive voltage is applied to the collector screen in front of the detector. With a negative voltage on the collector screen, a pure BSE signal is captured because the low-energy SEs is repelled. Electronscaptured by the scintillator/photomultiplier are then amplified for display on the viewing CRT. Although SEs and BSEs have been discussed here, any signal that can be collected and amplified may be used to form an image in the SEM (Goldstein et al. 2003: 24).

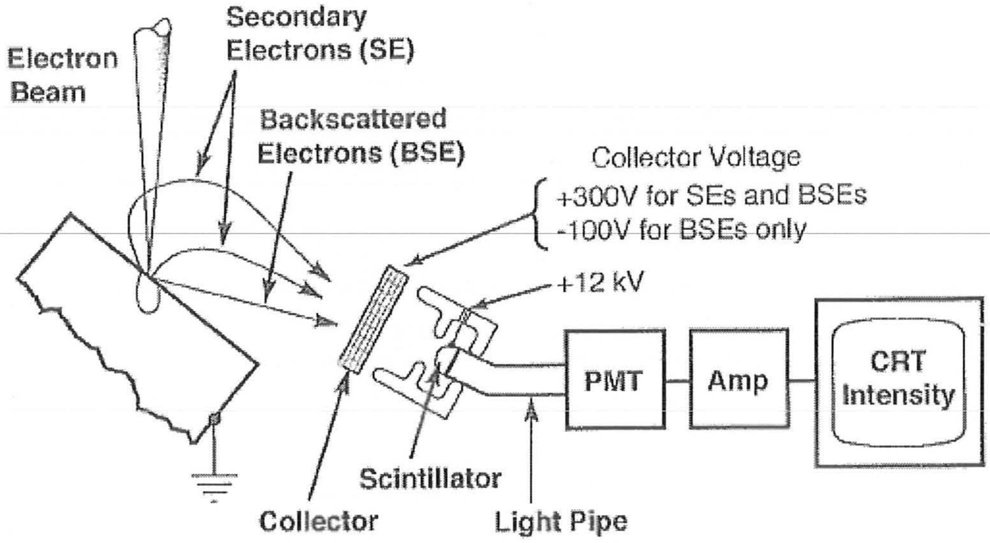

Figure 12: Diagram showing backscattered and secondary electron collection of these signals by the Everhart—Thornley (E—T) detector (Goldstein et al. 2003: 24)

Camera or Computer Records the Image

Older SEMs have a separate CRT for slow scan recording of images onto photographic film or, alternatively, a video printer to produce a hardcopy of the CRT image. Modern SEMs store their images in digital form in a computer for processing and printing at a later time (Goldstein et al. 2003: 25).

Operator Controls

The first controls that an operator must master are those that control the creation of the electron beam: the accelerating voltage and the emission current. Next come the lens controls: the condenser lens control determines both the amount of beam current available and the minimum beam size, and the objective lens control allows the beam to be focused so that the smallest diameter is located exactly at the specimen surface. Finally, because some locations on the specimen surface may appear too light or too dark on the viewing screen, signal controls, labelled contrast (or "dark level") and brightness, are provided to trim or expand the displayed intensity until a reasonable image is shown on the viewing screen. Observing the signal trace (line scan waveform) on an oscilloscope is a valuable means of understanding the action of these controls.; Note that whereas focusing is an activity similar to that on the light microscope, frequent adjustments of the contrast and brightness between focusing operations are also required on the SEM to produce an image on the screen (Goldstein et al. 2003: 25).

Sample Collection and Selection

Usually sample collection is not a problem as investigators bring their samples to the laboratory, but it is necessary to consider the problems involved in collecting and transporting specimens to the microscope. Large specimens may present a problem, and the best that can be done is to take a photograph of the whole sample to show what part of it was collected. For most inert dry samples, such as metals, rocks, geological specimens, wood, paper, fabrics, seeds, and most plastic and polymer specimens, it is only necessary to carefully wrap the specimen in clean dry material and place it into a secure well-labelled container. Powders, soils, and fine metal filings are more conveniently collected in clean containers or plastic bottles. More delicate samples should be wrapped in several layers of fine dry tissue. At this stage, no attempt should be made to clean the specimen other than to remove any excess surface liquid (Echlin 2009: 11).

Internal Dimensions of the SEM Specimen Chamber

The specimen chamber of the SEM is much larger than the specimen region of a transmission electron microscope (TEM). The specimen stages of most scanning electron microscopes are limited to examining every point on a specimen 5–10 cm in diameter. A number of factors limit the size of the specimen that may be examined in the SEM. The entrance to the microscope chamber must be large enough to allow the specimen to be placed on the specimen stage. For many SEM this does not present a problem because the entire specimen chamber is first vented to atmospheric pressure and the stage assembly is exposed in a draw-like fashion. Quite large specimens may then simply be placed onto the stage; the chamber is then closed and evacuated to its working pressure. In other microscopes, the mechanical parts of the stage assembly are maintained at high vacuum within the chamber volume and the specimen is inserted onto the stage through an air lock. This arrangement limits the size of specimens that may be put into the microscope for imaging and analysis. It is important to have a good understanding of the internal geometry of the specimen chamber of the SEM being used for microscopy and analysis. The dimension, position, and size of the final lens must be known. It is necessary to know the position of the specimen stage and how much it can be moved in the X, Y, Z, and tilt directions. It is important that the operator knows where the secondary and back scattered electron detectors and the energy dispersive x-ray detectors are located in the chamber and how much these may be moved. The secondary electron detector is usually in a fixed position at the edge of the chamber and the demountable solid state backscattered detector usually surrounds the final pole piece. The position of the backscattered detector may limit the shortest working distance between the sample surface and the final lens to 3–5 mm. The movable x-ray detector is usually located to one side of the chamber and only moved close to the sample during microanalysis. The position and subtending angle of the detector must be known to avoid large sample crashing onto the front of the detector. Short working distances associated with high-resolution images. A mid-working distance is used for most general SEM and, with the FEI XL-30, for x-ray microanalysis. The long working distance is used to provide an increased depth of field in order to view complexly sculptured specimens. The non-conductive specimen quickly charges and reflects the incoming electrons to the internal surface of the microscope, which provides a highly distorted image that shows the location and relative position of various chamber components. These types of images, together with the manufacturer's instructions and information, let the operator know how much space is available for a specimen inside the microscope column and how far it may be moved. For example, with a 2- to 5-mmthick flat specimen, the standard stage of an FEI XL-30 microscope can be moved 50 mm in the X and Y direction and the working distance moved 30 to 5 mm. Using a retractable x-ray detector; it is possible to safely examine a 25-mm cube of material (Echlin 2009: 12-17).

Microscope Operating Conditions

Having established the spatial parameters of all the components inside the microscope, it is important to establish precisely what sort of information about the specimen is needed. Magnification, resolution, and depth of focus are determined to a large extent by the working distance between the specimen and the final lens and the position of the signal detectors. It is necessary when using long working distance to examine a large specimen, to avoid touching any internal component inside the microscope. Long working distances reduce resolution but enhance the depth of focus when examining a highly convoluted sample at low magnification. If high-resolution images are required it is necessary to use a much smaller specimen that can be moved closer to the final lens. It may also be necessary to tilt the sample toward the x-ray detector in order to improve the take-off angle of the emitted x-ray photons (Echlin 2009: 17).

Sample Size

Most specimens examined in the SEM are much smaller than the dimensions mentioned in the previous paragraphs and usually conveniently fit onto the so-called Cambridge specimen stub, which is 12 mm in diameter and 3 mm thick. The general approach is to make the specimen as small as possible without compromising the appearance of the features of interest and the ability of the microscope to image and analyze these features (Echlin 2009: 17).

Large Specimens

Sometimes it is not possible to cut a very large specimen, such as a piece of rock, down to a convenient size without damaging the material. It can be argued that a large specimen gives a more representative view of the material being examined. Large biological samples have their own set of problems. Such samples invariably need stabilization prior to examination in the SEM. This stabilizations time dependent. The larger the sample, the longer it takes to stabilize. The same problem occurs when it is necessary to dry the specimen. Large porous samples such as some plastics, fabrics, and minerals may take a long time to pump out inside the microscope in order to reach the optimum high vacuum (Echlin 2009: 17).

Small Specimens

Although smaller samples generally are easier to handle than large specimens, there is one disadvantage to their reduced size. It is important to be certain that the small sample that has been separated from a much larger sample is representative of the whole specimen. This problem is not unique to the SEM but is one of the disadvantages of any reductive analysis process. Onaway around this conundrum is to examine a larger number of smaller samples taken from the same specimen (Echlin 2009: 18).

Sample View

The SEM is designed to obtain information from the very surface of specimens. This information may come either from the natural surface of the specimen or from a surface that has been exposed by artificial means to reveal the interior of the sample. A decision should be made early in the process of sample preparation about the proposed examination of the specimen (Echlin 2009: 18).

Sample Labelling

It is vital that the SEM specimen is properly labelled. It is rarely possible to label the specimen directly, but this approach can be achieved with an indelible marker on the underside of metal specimen. There are a number of marking systems, but an alpha numeric code is straightforward. The sample label should be quite unique and should follow the sample throughout the process of sample selection to the final image or data set. The same unique code should be used in the accompanying mandatory laboratory notebook, which should have recorded details of everything that has happened to the sample. If it is not immediately possible to label the sample directly, it should be kept in a labelled container. At the stage in the preparation procedure in which the sample is firmly attached to the specimen holder, the unique label should be firmly attached to the underside of the specimen holder. In this way, the identity of the specimen will not be lost, particularly in conditions in which several different samples are placed on the same specimen stage (Echlin 2009: 18).

Sample Preparation Tools

Specimen Size

It is important to produce samples that will fit inside a SEM. Most non-specialized scanning microscopes, although they can handle specimens up to 50 mm diameter and 20 mm thick, usually examine much smaller samples that can fit either on the 12-mm diameter, so-called Cambridge support or stub, or the larger, 25.4-mm (1-in.) (Echlin 2009: 20-21).

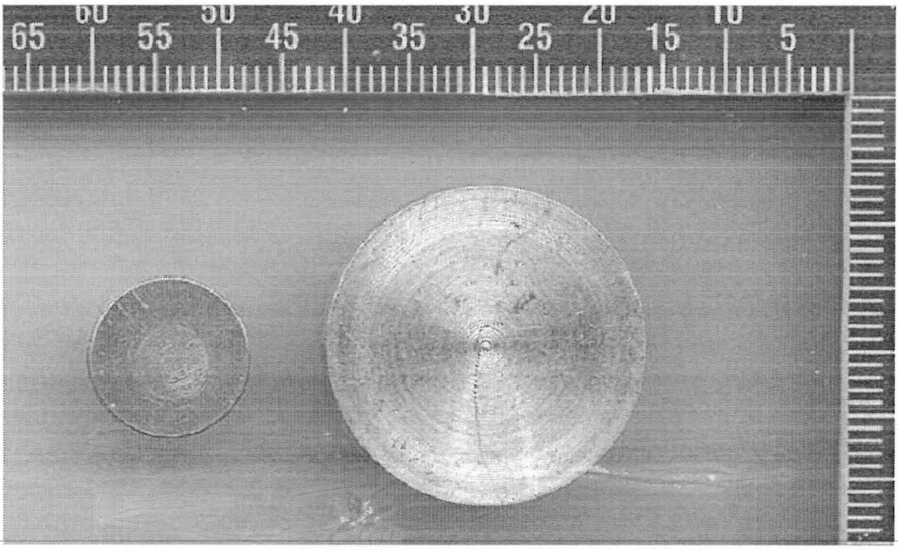

Figure 13: 12- and 24.5-mm aluminium specimen stubs (Echlin 2009: 20).

General SEM Sample Preparation Laboratory

There must be separate wet and dry areas; a low-vibration area for sensitive equipment; a region set aside for sputter and evaporative coatings; spark-free storage cupboards and fume chambers; drying ovens and ultrasonic cleaners; plenty of cupboards and shelves; a region set aside for any pieces of specialized equipment; and secure places to tether high-pressure gas bottles, such as those containing nitrogen, carbon dioxide, and argon. The whole laboratory should be well lit and ventilated, and fitted with plenty of electrical power points and appropriate laboratory furniture, including comfortable chairs. There must be separate waste bins for glass and sharps, toxic and hazardous material, and general waste. All these pieces of equipment and the general arrangement and operation of the laboratory must meet the Health and Safety regulations in force in a particular country, as some of the chemicals and many of the operations involved ensample preparation are potentially hazardous. As far as appropriate, specimen preparation should be carried out on a firm bench with a comfortable adjustable chair, because small hand-held tools must be held securely. For very small specimens it may be necessary to use a micromanipulator to hold and move the tools (Echlin 2009: 21-22).

Equipment to Facilitate Looking at the Process of Sample Preparation

A few larger pieces of equipment facilitate specimen preparation, particularly for smaller samples. It is useful to have a good quality100-mm diameter glass hand lens with a magnification of ×5 that can be fixed to an adjustable support and is close to a pair of flexible light sources. Smaller × 10 magnification hand-held lenses useful for inspecting the sample more closely. Easy access to a good binocular light microscope is an additional advantage (Echlin 2009: 22).

Tools to Expose Samples

Grinders, Saws, and Cutters for Hard Samples

The size of these tools depends very much on the size of the specimen being studied. Choose the size, form, and power for the expected type of specimen. Dental burrs are an excellent way to trim and grind small samples of hard material (Echlin 2009: 22).

Blades, Knives, and Scissors for Soft Samples

Sharp surgical knives and disposable scalpel blades of various shapes and size are available from a number of different supply houses. Disposable razor blades are very effective for cutting away larger pieces of soft material, but it is important to first wipe the surface with acetone to remove the fine layer of oil. Very thin stainless steel razor blades can be cut to size using scissors and then held in a metal holder (Echlin 2009: 22).

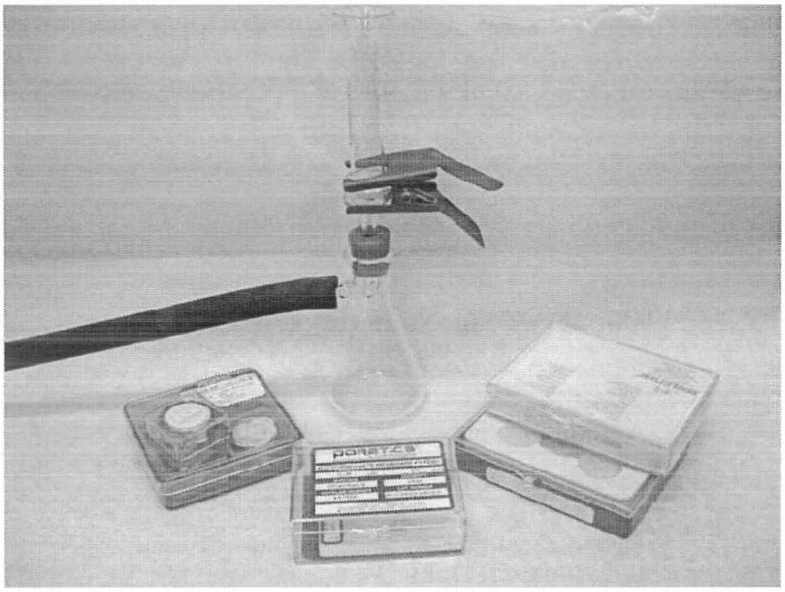

Figure 14: Filtration apparatus and filters composed of a system that allows a liquid suspension to pass through filters of various size designed to retain solids of different sizes and compositions (Echlin 2009: 22).

Fine-Pointed Probes, Needles, and Brushes

Dental probes are suitable to expose hidden parts of the sample. Sewing needles may be used to pick up small specimens and move them to the sample holder. Fractured tungsten wire provides very fine-pointed needles and the fine fresh needles used in acupuncture are sterile and have very fine points. Small disposable needles can be held conveniently in metal holders. In addition to the metal needles and probes, wooden applicator sticks, toothpicks, fine glass needles, and even some plant prickles, thorns, and spines can be used to manipulate small samples (Echlin 2009: 24).

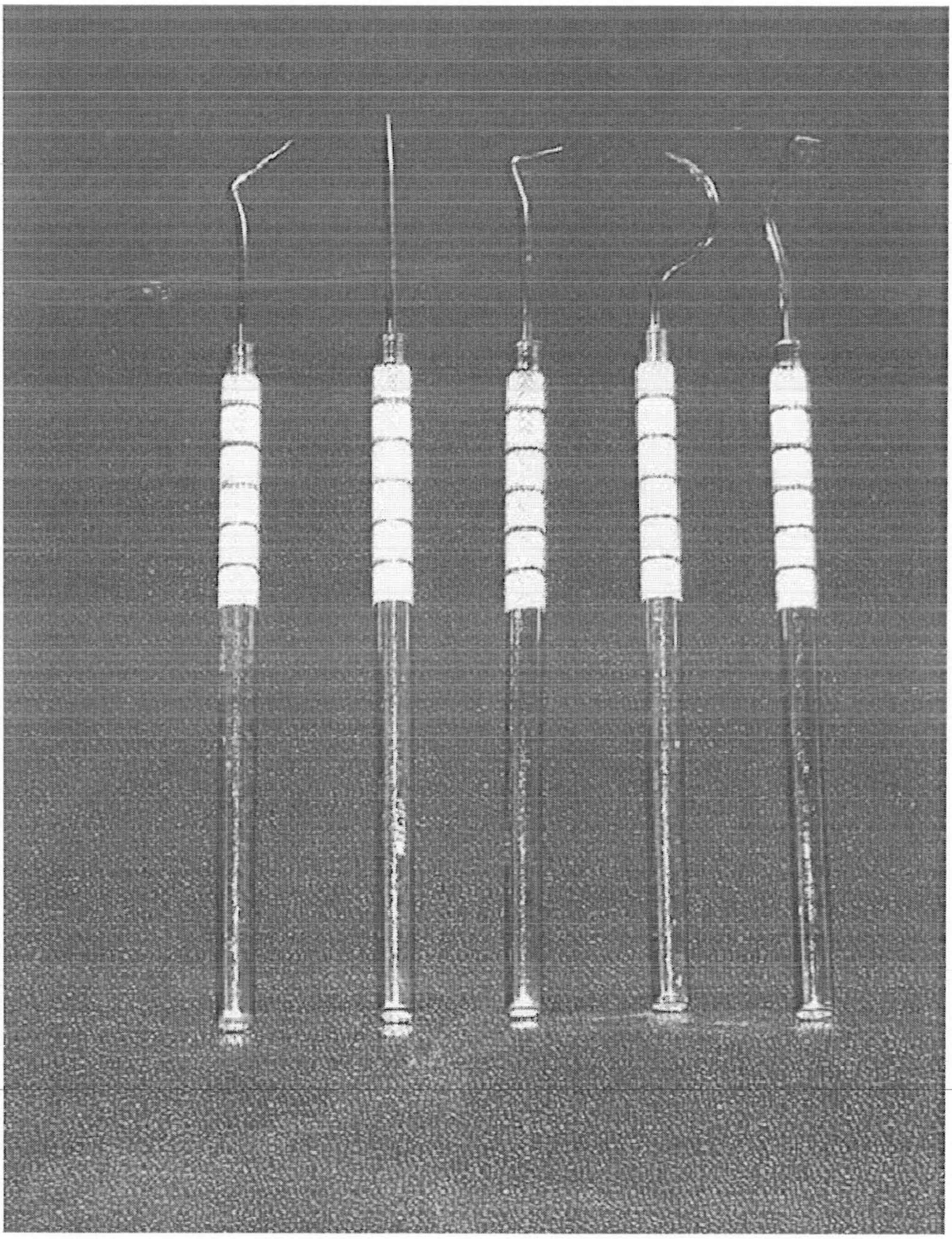

Figure 15: A set of stainless steel dental probes (Echlin 2009: 24).

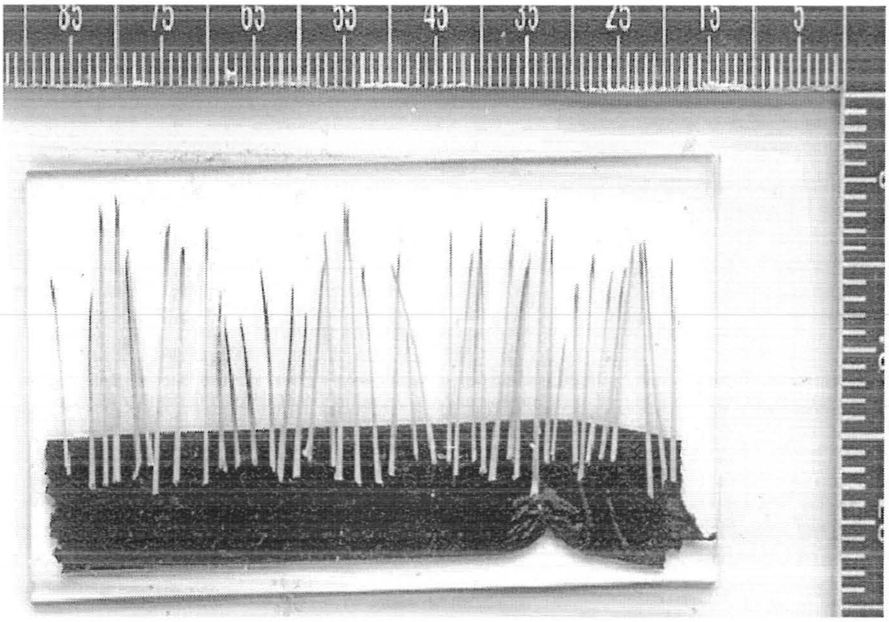

Figure 16: A collections of cactus needles that may be used as inexpensive disposable probes (Echlin 2009: 25)

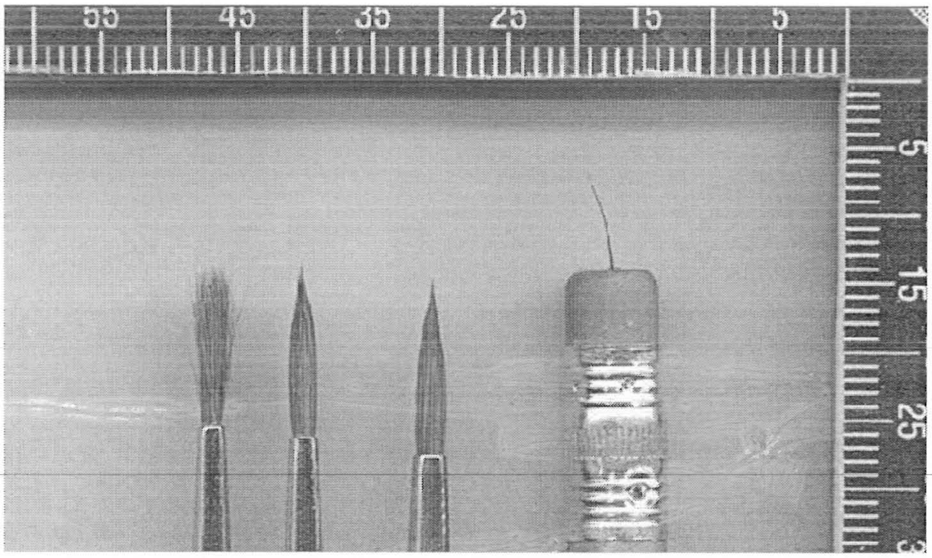

Figure 17: A collection of sable hair brushes (bulk and trimmed) and a single pig's eyelash "probe" inserted in a pencil eraser (Echlin 2009: 25)

Tools to Hold Large Samples

Larger hard specimens may be clamped in a mini vice; soft specimens may be impaled on fine metal points. Forceps are convenient way to temporarily hold and move specimens. Small and large spring-loaded surgical forceps are capable of holding large samples and picking up and holding small samples. Fine pointed spring loaded forceps are well suited for picking up particles as small as 100 μm (Echlin 2009: 26).

Tools to Help Clean Samples

- Brushes: Small 2- to 4-mm diameter natural hair or nylon brushes can be used to sweep away dust and particles on the surface of specimens but they should not be used to paint the sides of non-conducting samples with silver or carbon paint.
- Wooden tooth picks are much better adapted to this activity. In addition to brushes, it is helpful to have a small container of compressed gas with a fine nozzle that can blow away fine dry particles.
- Pipettes. It is sometimes necessary to flush or irrigate a region of the specimen; and fine plastic pipettes with an integrated teat are ideal for this purpose. Fine glass pipettes can be drawn to size from flame-heated glass tubes, but care must be taken not to damage the surface of delicate samples (Echlin 2009: 26).

A Personal Set of Specimen Preparation Tools and Associated Perquisites

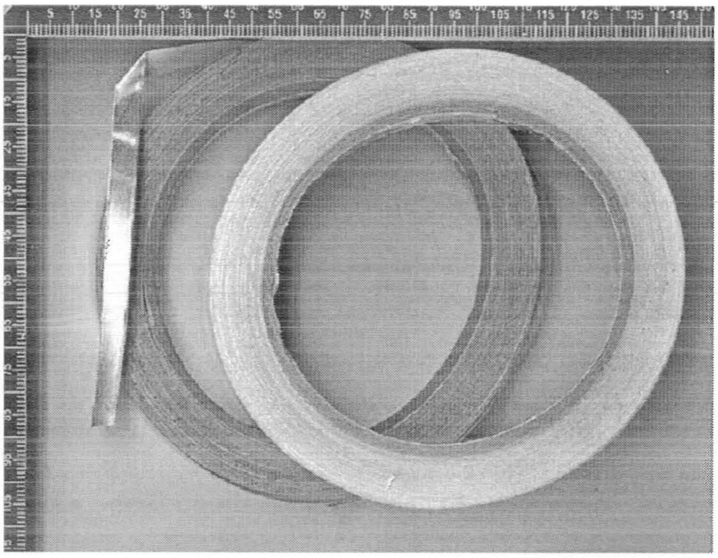

Figure 18: Aluminium and copper tape, double-sided and coated with organic adhesive (Echlin 2009: 27).

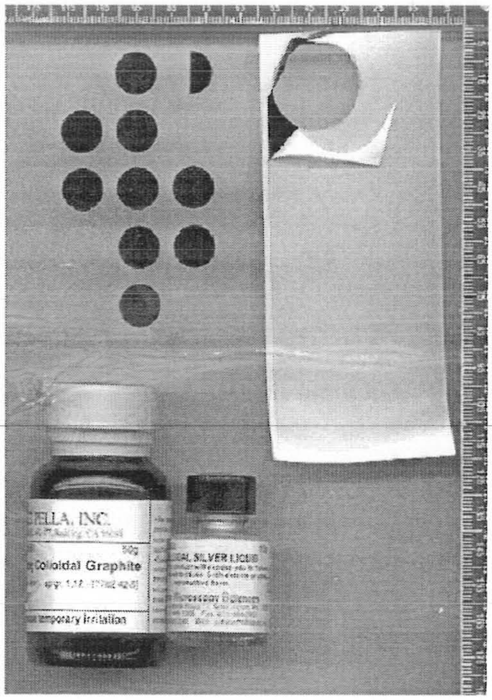

Figure 19: Ten-millimetre-diameter carbon mounts with a double-sided coating of an organic adhesive (Echlin 2009: 27).

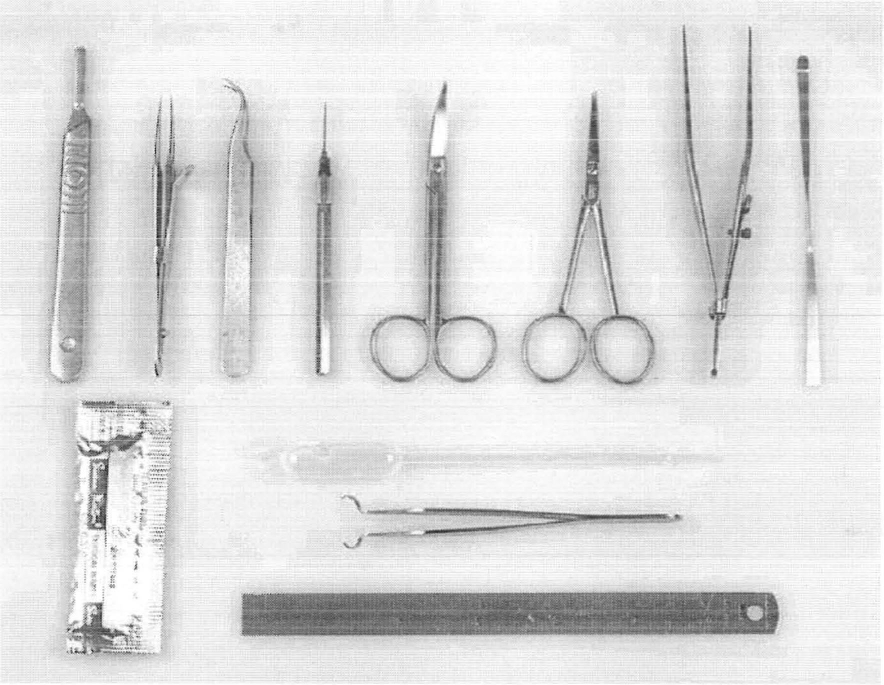

Figure 20: Other Tools for Sampling (Echlin 2009: 28).

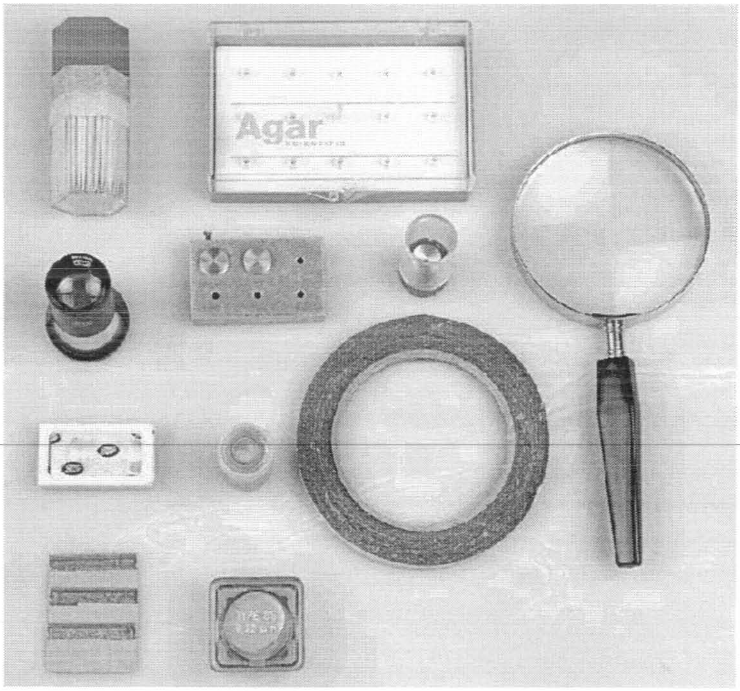

Figure 21: Other Tools for Sampling (Echlin 2009: 28).

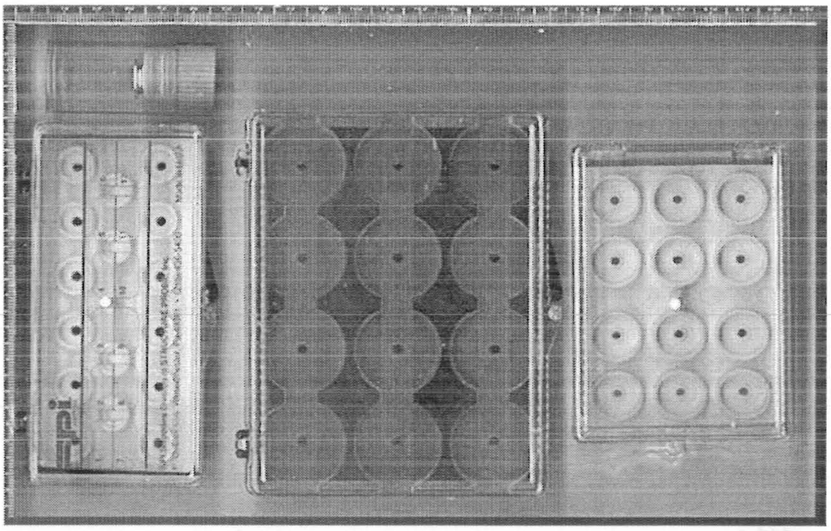

Figure 22: Top left. A small plastic sealed container is for an individual 12-mm Cambridge stub. Lower left and right. These flat storage containers are suitable for storing many 12-mm stubs. Middle. The storage box can be used to store flat 12-mm-diameter carbon planchets or flat metal stubs. Specimen boxes have secure lids to ensure sample free of dust and moisture. The boxes must be labelled (Echlin 2009: 29).

Part 3

Scanning Electron Microscopy of the Archaeological Material of District Shangla

Apparatus

Scanning Electron Microscope, specimen stub, Grinder, Saw, Cutter, Fine-Pointed Probe, Needle, and Brush.

Procedure

The following sample is acquired from the Kandaro site, Bilkanai, Alpurai, District Shangla, Pakistan. First of all the researcher divided the sample to 6-inch pieces with the help of tools, as mentioned previously in Part 2, in order to fit the sample pieces in the specimen chamber. The sample was then coated with electrically conducting material by low-vacuum sputter. The sample is then placed in the specimen chamber to obtain computerized result.

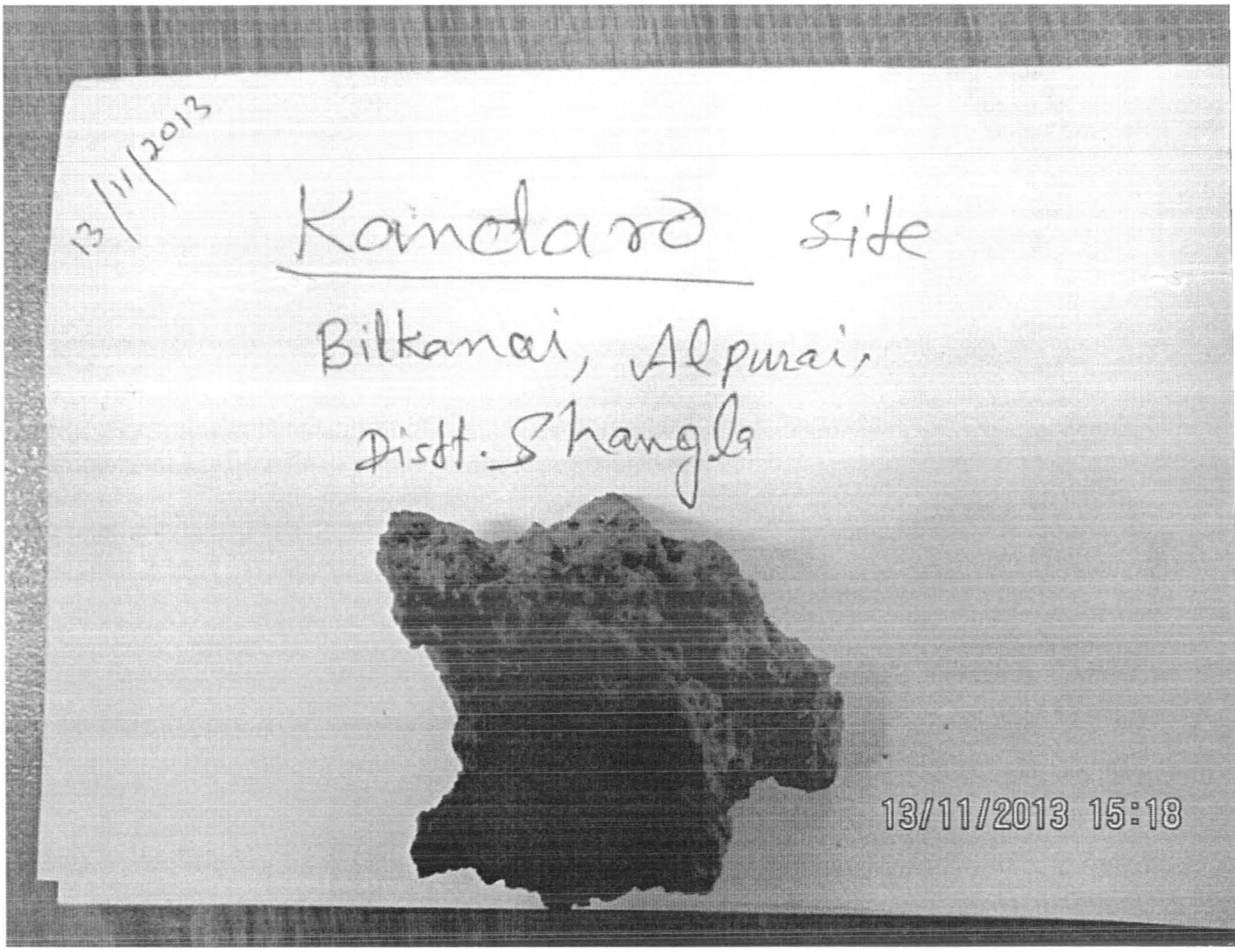

Figure 23: Archaeological sample for SEM

Results

```
Title          : IMG1
----------------------------
Instrument     : 6490(LA)
Volt           : 20.00 kV
Mag.           : x 50
Date           : 2013/12/05
Pixel          : 512 x 384
```

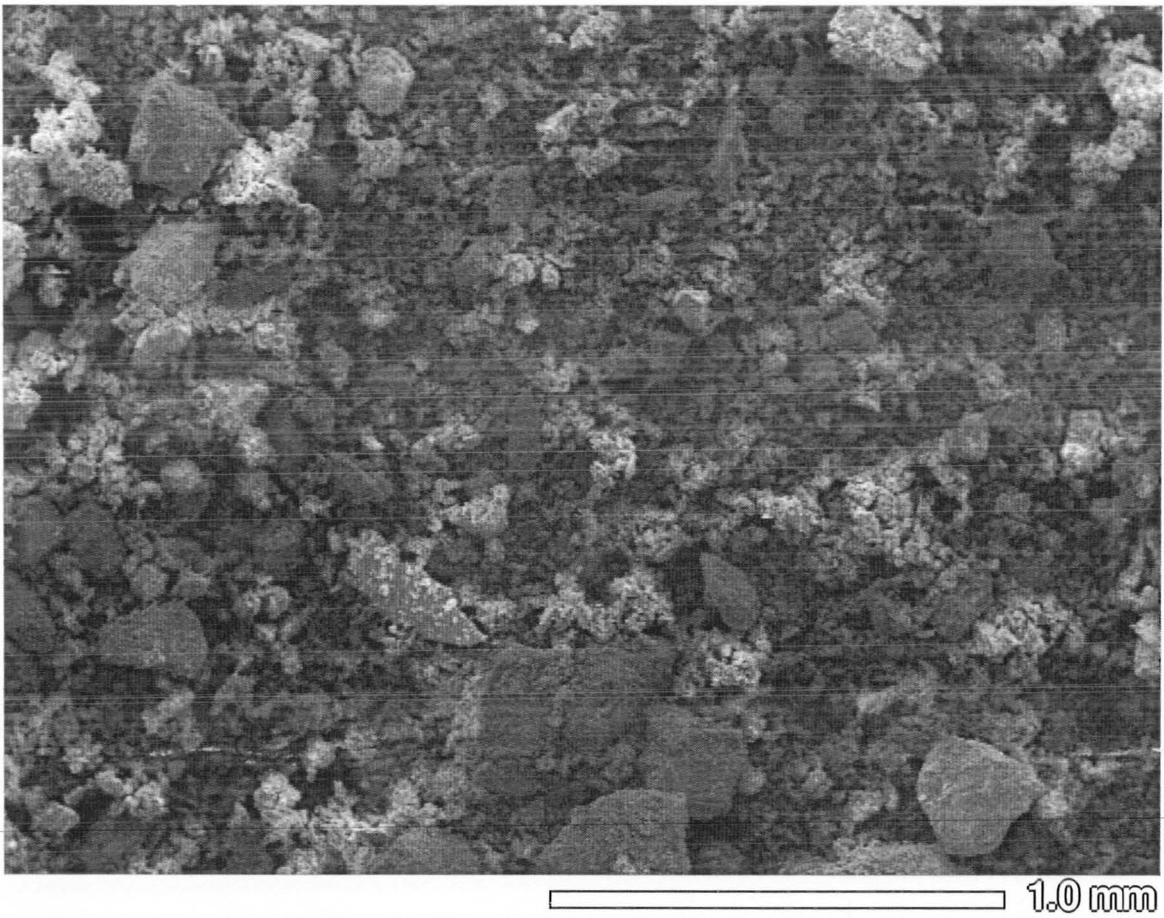

Figure 24: The sample is mixture of different type of elements. mm Image obtained from the SEM shows the composition of the sample. The resolution of the image is 512 x 384 pixels with 50x magnification.

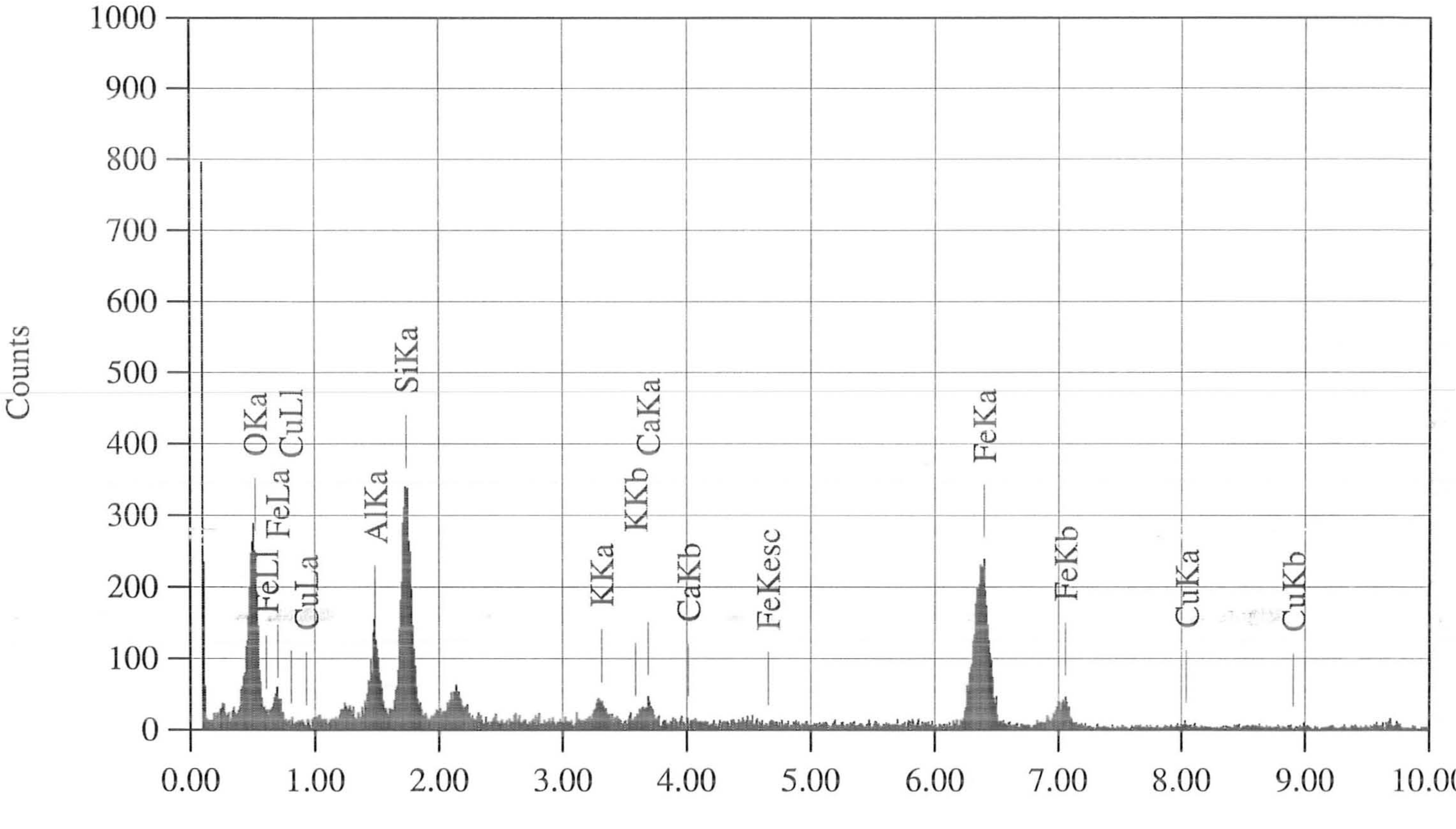

Figure 25: Graph of SEM

The above peaks show that the sample contains seven elements and their percentage is different. The composition of the sample can be cleared from the following graph. Red colour shows the presence of iron. The higher is the peak, the higher the percentage of the element in the sample. It is a computerized result created by SEM.

```
ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.6296

Element        (keV)   Mass%  Error%   Atom%  Compound    Mass%  Cation          K

 O K           0.525   28.42    0.80   50.40                               32.0959

Al K           1.486    6.94    0.71    7.30                                4.2547

Si K           1.739   17.63    0.68   17.81                               12.8327

 K K           3.312    1.54    0.68    1.12                                1.7680

Ca K           3.690    1.89    0.77    1.34                                2.3168

Fe K           6.398   41.82    1.66   21.25                               44.9910

Cu K           8.040    1.76    3.55    0.79                                1.7409

Total                 100.00          100.00
```

Table. No. 9: Elemental Composition of the Sample

The sample is consisted of oxygen (O, 28.42%), aluminium (Al, 6.94%), silicon (Si, 17.63%), potassium (K, 1.54%), calcium (Ca, 1.89%), iron (Fe, 41.82%) and copper (Cu, 1.76%). High percentage of iron shows that the sample is an iron ore. A lot of such samples has been obtained from the site. This is a clue that there was metallurgy at the site. Excavation is needed to obtain more archaeological data.

CHAPTER 3

X-Ray Diffraction of the Pottery of Shere Pate, Kafiro Dherai, and Sar Pati, District Shangla

X-ray diffraction (XRD) from the solid state is a fundamental technique for the characterization of synthetic and natural materials. Since the discovery of Bragg-type X-ray diffraction from periodic crystal lattices, the technique has proven an essential tool for: (1) the identification of crystalline compounds, (2) the quantitative analysis of polyphasic mixtures, (3) the study of the long-range atomic structure of crystals, including detailed charge density studies, and (4) the physical analysis of crystalline aggregates, including orientation texture, crystallite size distribution, and lattice micro-strain effects. During the first half the last century such routine applications were developed into standard analysis procedures, and during the last decades they became so widely used that data are now available for most known inorganic compounds and minerals, to the extent that electronic databases are now accessible for automatic identification and rapid retrieval of crystallographic and structural information of crystalline substances. The routine identification or quantification of crystalline phases by diffraction is by far the most widespread application in archaeometry, although non-destructive analysis of a material's texture has recently been proven to be a powerful tool especially in metal investigations. The focus of modern crystallographic research on inorganic solids is the interpretation of the physical and chemical properties of materials in terms of their ideal or defective atomic structure, and the transfer of the acquired crystal chemical knowledge to the engineering of solid state compounds with novel technological properties. The last twenty years have also witnessed the development of dedicated second and third generation synchrotron radiation sources in the region of hard X-rays. The availability of brilliant, polarized, and collimated synchrotron radiation beams with a wavelength that is tunable over a wide spectral range has made a number of interesting advances possible in materials characterization. State-of-the-art investigations of inorganic compounds and minerals by synchrotron X-ray diffraction include in situ dynamic diffraction of kinetic processes and phase transformations, structural characterization of compounds at ultra-high pressures, and the use of resonant scattering effects for element-selective structural analysis. None of these advanced applications has yet found direct archaeometric applications, with only high temperature diffraction being sometimes used as a novel tool for in situ triggering of the reactions taking place during the firing of old ceramics, with the aim of reconstructing the original firing temperatures. XRD data collection and analysis is routinely performed in any laboratory dealing with inorganic or mineral compounds. Samples are commonly in the form of small single crystals (with sizes in the range 0.1–1.0 mm), polycrystalline aggregates (powders, i.e. assemblages of 103–106 crystallites with size around 1 mm), or oriented specimens (fibres, thin films, polished surfaces). Therefore the experimental techniques and data analysis methods to be applied may vary, depending on the physical state and the chemical composition of the sample besides, of course, the nature of the requested information. Typical laboratory applications in inorganic chemistry, solid state physics and mineralogy may involve: (1) the identification of unknown crystalline phases, (2) the quantification of phase abundance in polycrystalline mixtures, (3) crystal structure determination and refinement, (4) physical analysis of the sample in terms of crystallite size, lattice micro-strain, or orientation texture of the crystal domains. In archaeometry, XRD easily represents the cheapest and most reliable technique for identifying crystalline phases both in natural and man-made materials such as metals, metal slags, ceramics, soils, building stones, pigments, plasters, etc. The experimental apparatuses commonly involve a sealed-tube or rotating anode X-ray source, a 2-circles (for powders) or a 4-circles (for single crystals) automated diffractometer for sample orientation with respect to the incident beam, and one or more detector banks for detection of the diffracted signal. The data collected are generally intensity profiles of the diffracted X-rays as a function of the scattering angle which shows the Braggdiffracted peaks characteristic of each crystalline phase. The angular position, the integrated intensity, and the peak profile shape of the diffracted signal are important for the subsequent analysis based on Bragg's Law (2d sin q = nλ) where d is the distance between lattice planes in the crystal, q is half the diffraction angle between the incident and diffracted beams, and λ is the wavelength of the incoming radiation (Artioli 2010: 50-51).

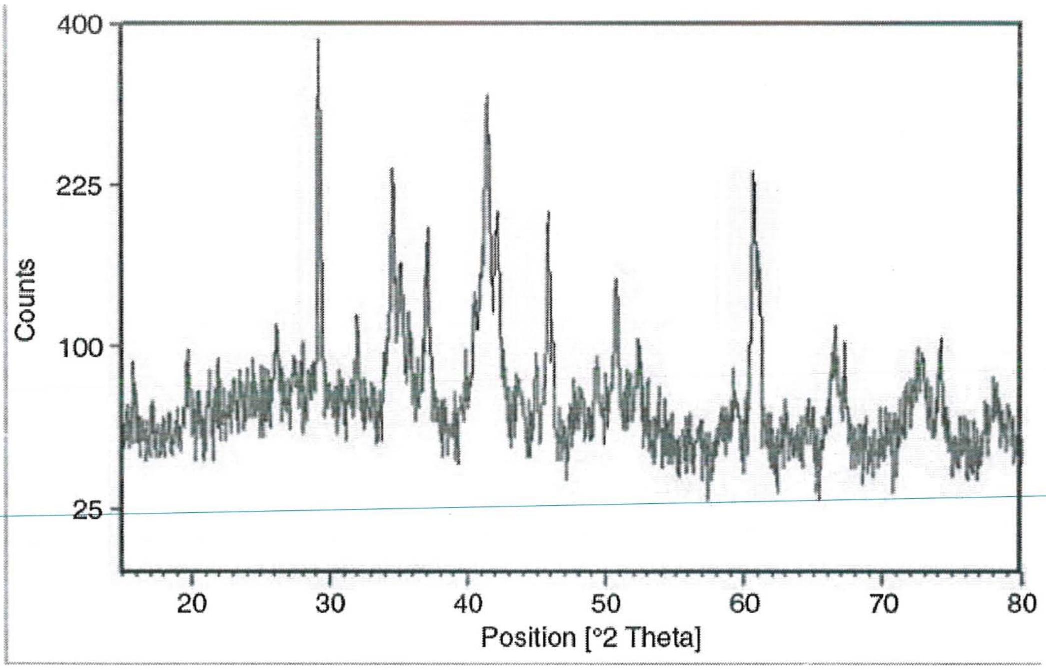

Figure 26: Typical X-ray diffraction powder pattern obtained by a laboratory 2-circle diffractometer on a poorly diffracting sample. The visible Bragg's diffraction peaks are used to identify and quantify the crystalline phases in the sample (Artioli 2010: 51)

Crystal Systems

Crystal system	Cell lengths	Cell angles
Cubic	a=b=c	α=β=γ=90°
Tetragonal	a=b, c	α=β=γ=90°
Orthorhombic	a, b, c	α=β=γ=90°
Hexagonal	a=b, c	α=β=90°, γ=120°
Rhombohedral	a=b=c	α=β=γ
Monoclinic	a, b, c	α, β=γ=90°
Triclinic	a, b, c	α, β,γ

Table No. 10. 7 types of crystal systems: (Mitchell n.d: 7)

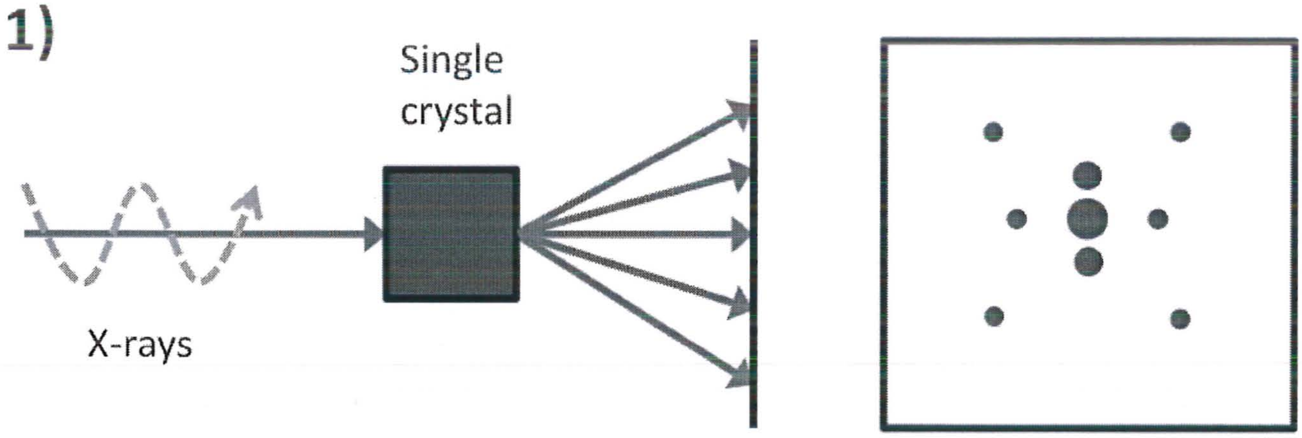

Figure 27: Single crystals: X-rays diffracted from a single crystal produce a series of spots in a sphere around the crystal. Each diffraction peak uniquely resolved (Mitchell n.d: 16)

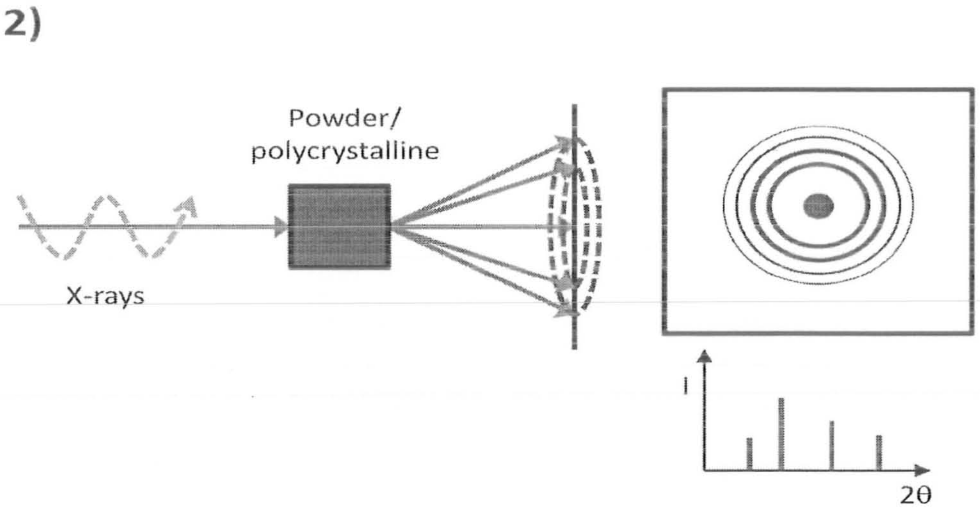

Figure 28: Powders: Linear diffraction pattern with discrete "reflections" obtained by scanning through arc that intersects each debye cone at a single point (Mitchell n.d: 16)

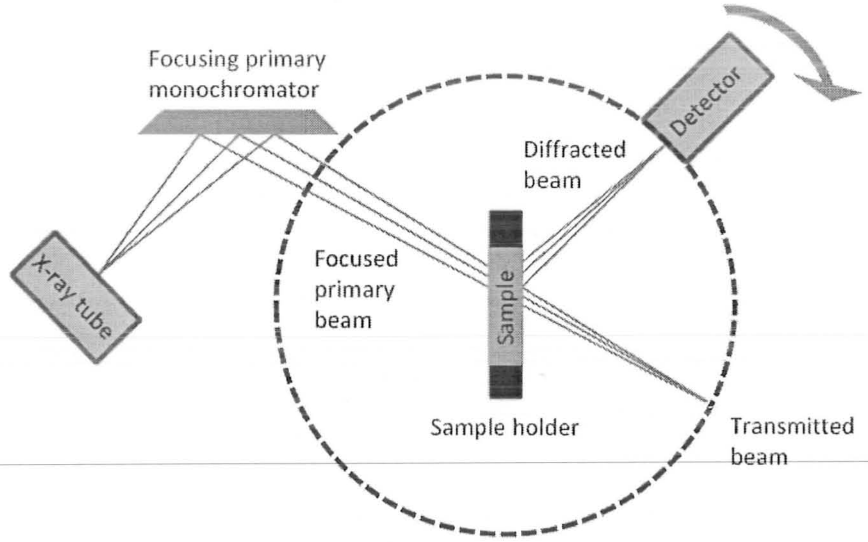

Figure 29: Geometry of Defractometer (Mitchell n.d: 26)

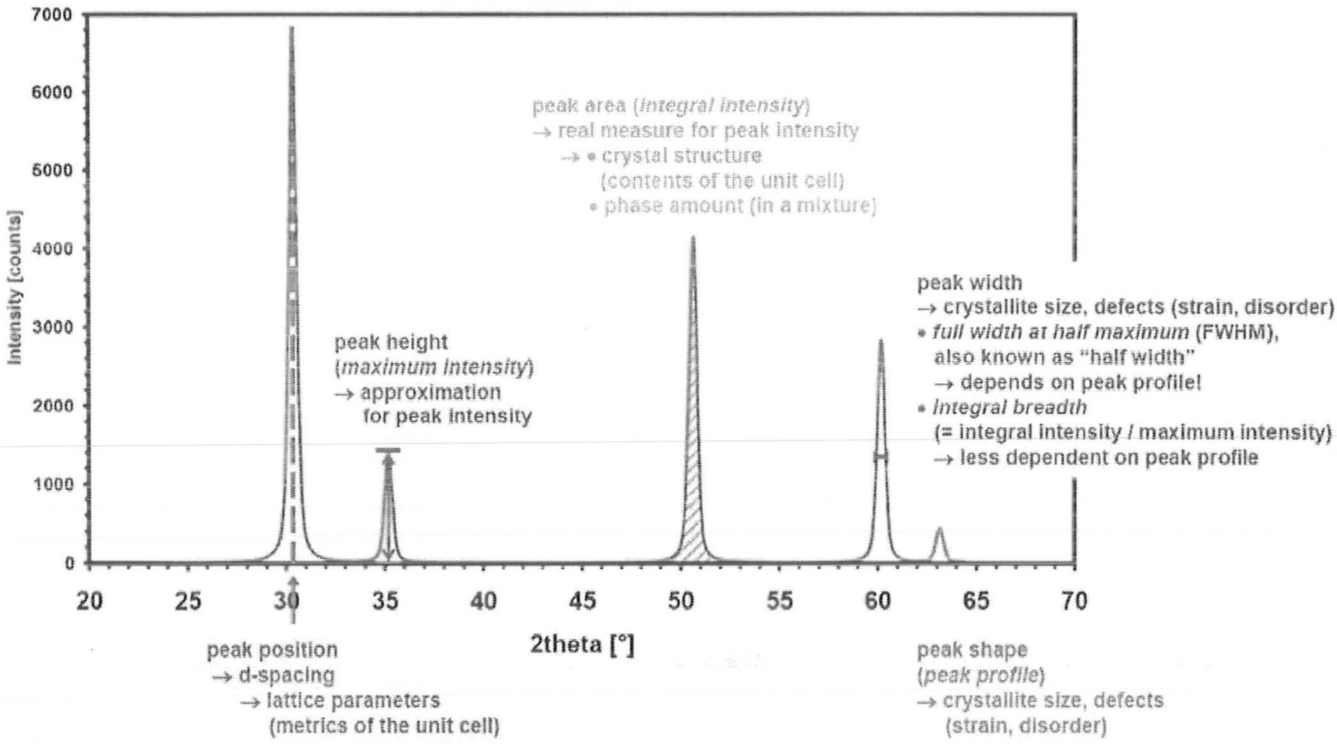

Figure 30: "Anatomy" of the XRD pattern (Mitchell n.d: 28)

In practice, for essentially all known minerals, the angles at which they diffract X-rays are known and tabulated in searchable databases. Modern diffract meters commonly use such databases to match the pattern obtained from an unknown sample to specific minerals, removing the need for calculating the crystal dimensions. In an actual application, a small sample, 5–10 mg or more, would be taken from an artefact and crushed to a powder and mounted in the middle of the diffractometer. As the detector, rotates around the sample, the computer counts the intensity of the X-rays at each angle. The angles at which the sample diffracts X-rays are then listed, along with their relative intensities, and compared to those in the searchable database. The computer then presents the closest matches to know minerals. In the example here, the material frogman archaeological stone bowl is identified as the mineral chlinochlore (Price and Burton 2011: 120).

X-Ray Diffraction of the Pottery of Shere Pate, District Shangla (AC-1a)

No.	Pos. [°2Th.]	d-spacing [Å]	FWHM [°2Th.]	Rel. Int. [%]	Matched by	Backgr.[cts]	Height [cps]	Height [cts]
1	21.0841	4.21376	0.3542	15.79		0	36	9
2	26.9501	3.30843	0.1771	100		0	228	57
3	36.8313	2.44039	1.417	19.3		0	44	11
4	50.3938	1.81086	0.1771	29.82		1	68	17
5	60.1264	1.53893	0.7085	21.05		0	48	12
6	68.2557	1.37298	0.864	14.04		0	32	8

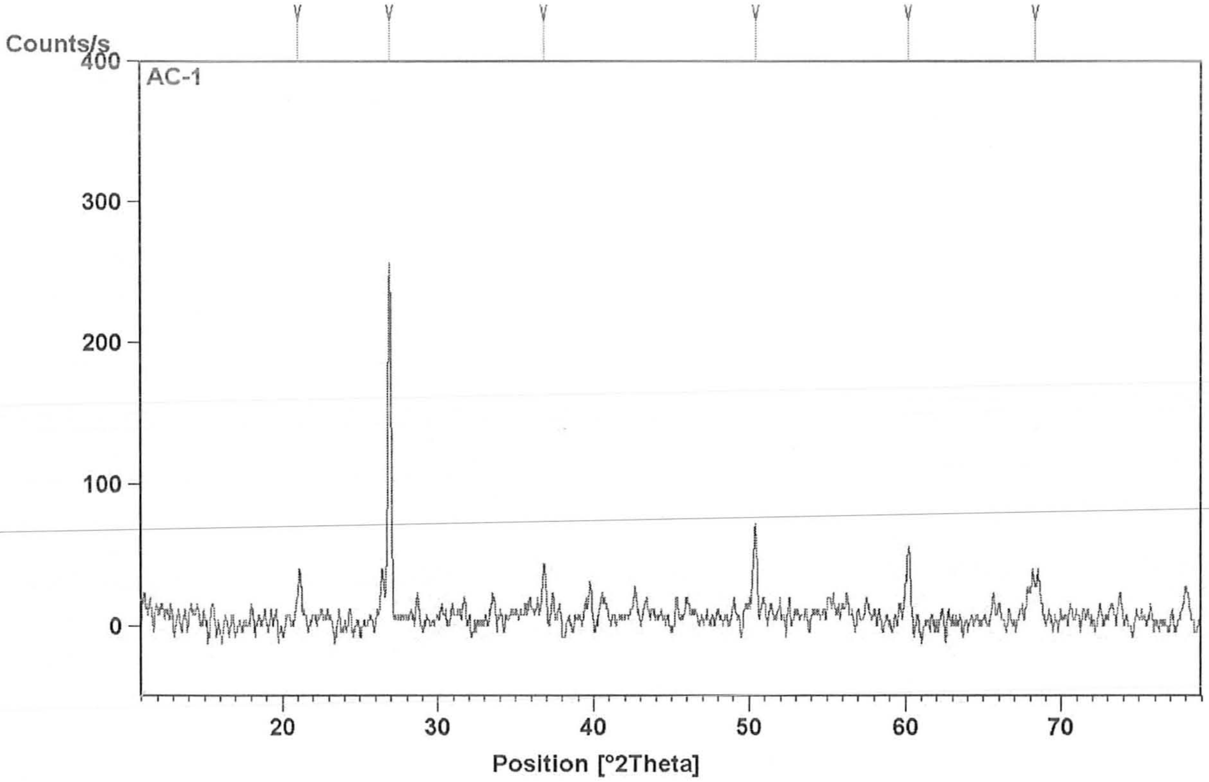

Figure 31: Morphology of the crystals present in the pottery power

X-Ray Diffraction of the Pottery of Kafiro Dherai, District Shangla (AC-2a)

No.	Pos. [°2Th.]	d-spacing [Å]	FWHM [°2Th.]	Rel. Int. [%]	Matched by	Backgr.[cts]	Height [cps]	Height [cts]
1	26.8678	3.31838	0.2066	100		1	440.16	110.
2	28.0708	3.17884	0.3542	11.36		1	49.99	12
3	36.5248	2.46016	1.417	5.38		0	23.66	5.
4	50.335	1.81284	0.2362	20.02		1	88.13	22.
5	60.0223	1.54136	0.7085	4.65		2	20.49	5.
6	68.3712	1.37094	0.432	16.23		1	71.45	17.

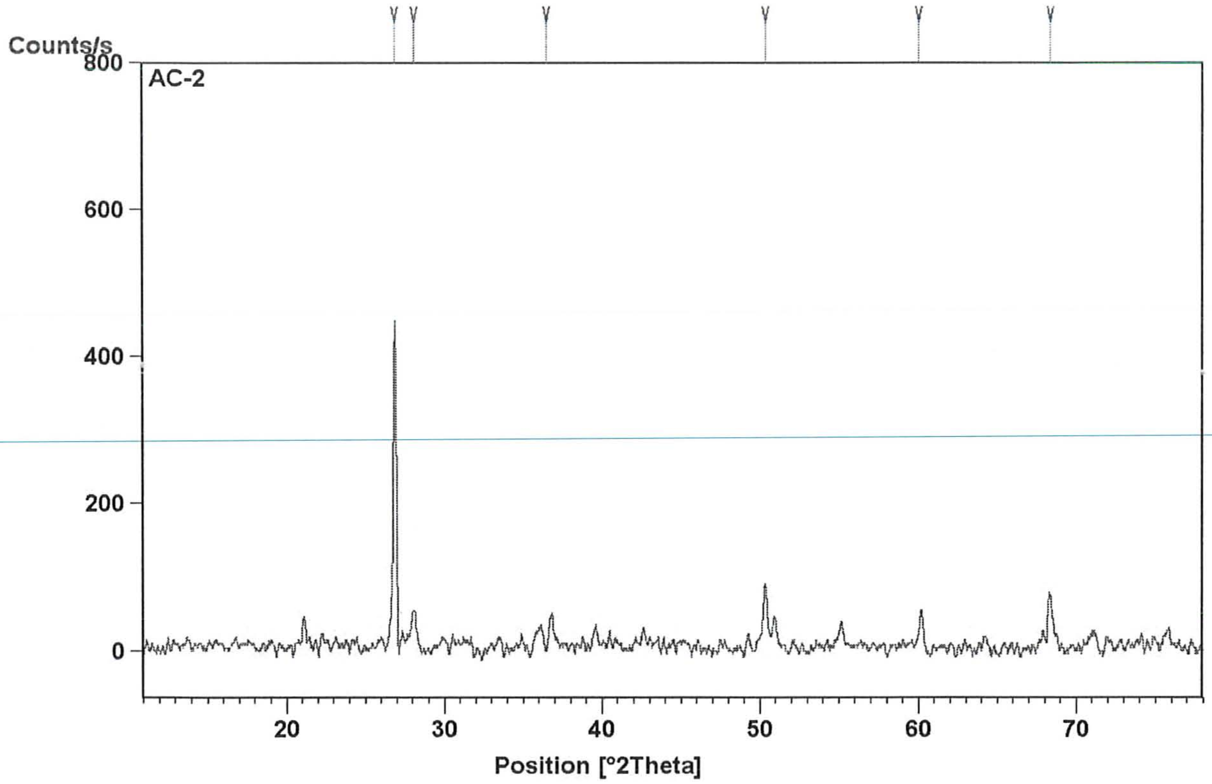

Figure 32: Morphology of the crystals present in the pottery power

X-Ray Diffraction of the Pottery of Shere Pate, District Shangla (AC-3b)

No.	Pos. [°2Th.]	d-spacing [Å]	FWHM [°2Th.]	Rel. Int. [%]	Matched by	Backgr.[cts]	Height [cps]	Height [cts]
1	21.3647	4.15905	0.3542	13.25		1	44	11
2	27.0799	3.29287	0.1476	100		-1	332	83
3	36.5285	2.45991	1.1808	3.61		-1	12	3
4	50.4675	1.80839	0.3542	15.66		0	52	13
5	68.278	1.37259	0.864	6.02		0	20	5

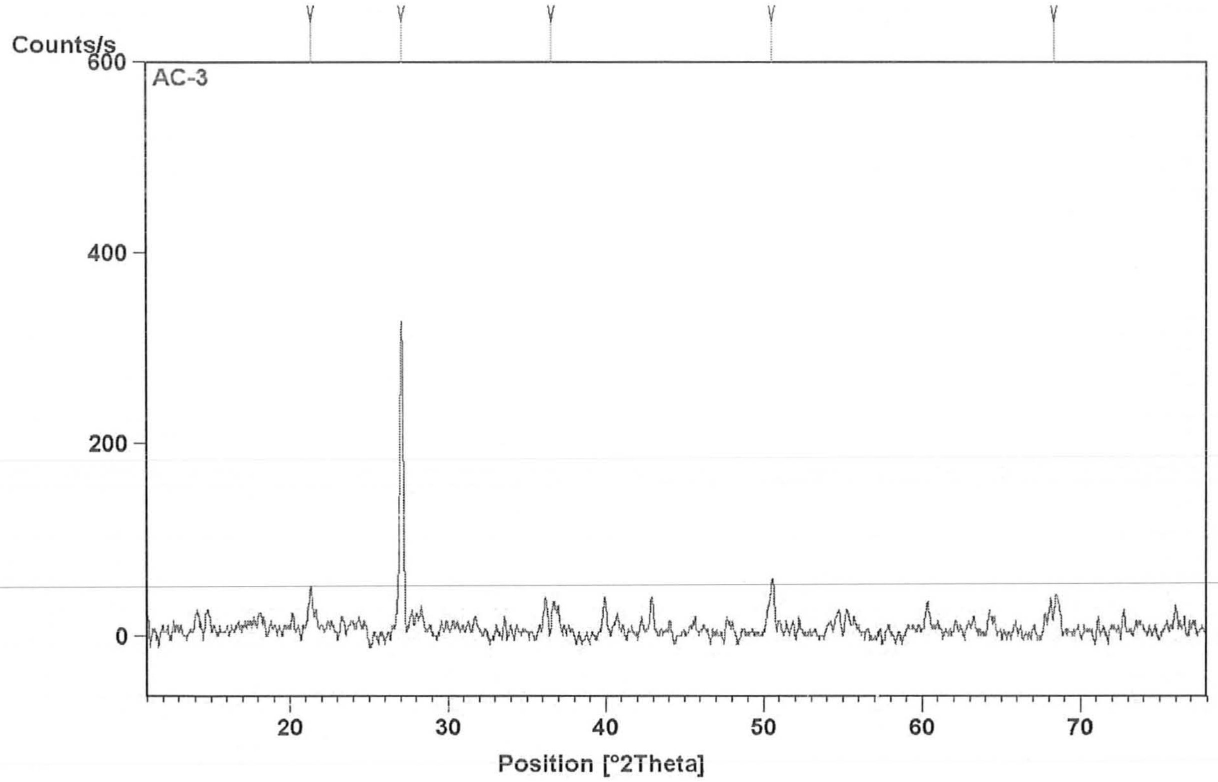

Figure 33: Morphology of the crystals present in the pottery power

X-Ray Diffraction of the Pottery of Sar Pati, District Shangla (AC-4)

No.	Pos. [°2Th.]	d-spacing [Å]	FWHM [°2Th.]	Rel. Int. [%]	Matched by	Backgr.[cts]	Height [cps]	Height [cts]
1	23.3728	3.80606	0.3542	2.24		0	28	7
2	29.7501	3.00312	0.0738	100		-2	1248	312
3	36.316	2.47382	0.1771	5.45		0	68	17
4	39.7857	2.26572	0.2066	10.58		0	132	33
5	43.536	2.07884	0.1181	11.54		0	144	36
6	47.9601	1.8969	0.2362	10.26		-1	128	32
7	48.9096	1.86228	0.1181	12.82		-1	160	40
8	56.9854	1.61606	0.3542	1.92		-1	24	6
9	57.8514	1.59392	0.2952	4.49		-1	56	14
10	61.3043	1.51216	0.7085	2.88		-1	36	9
11	65.0513	1.43383	0.3542	3.21		-1	40	10
12	65.9802	1.41588	0.3542	1.6		-1	20	5
13	69.6581	1.34985	0.3542	1.28		0	16	4
14	70.7934	1.33096	0.3542	2.24		0	28	7
15	73.3494	1.29077	0.3542	1.92		0	24	6
16	77.7099	1.22786	0.576	2.24		-1	28	7

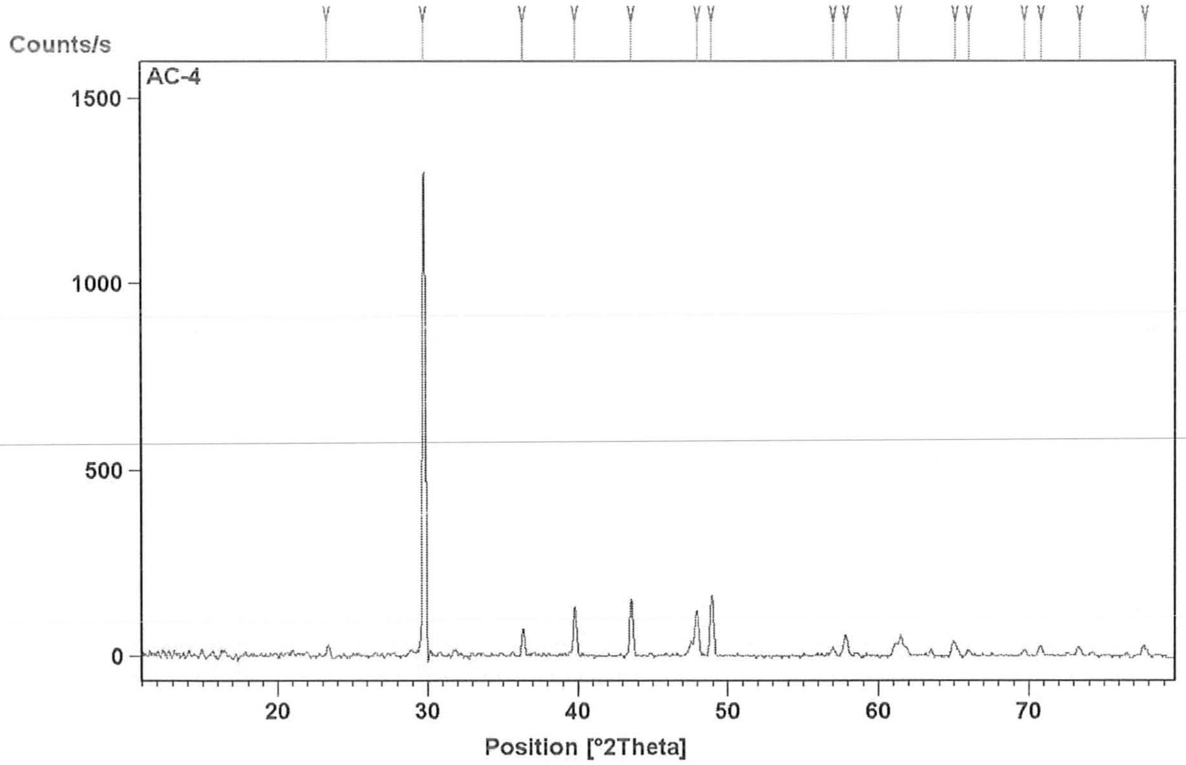

Figure 34: Morphology of the crystals present in the pottery power

X-Ray Diffraction of the Pottery of Kafiro Dherai, District Shangla (AC-5b)

No.	Pos. [°2Th.]	d-spacing [Å]	FWHM [°2Th.]	Rel. Int. [%]	Matched by	Backgr.[cts]	Height [cps]	Height [cts]
1	26.8477	3.32082	0.2657	100		0	523.59	130.9
2	50.4204	1.80997	0.2066	19.09		0	99.94	24.98
3	60.1868	1.53754	0.3542	9.2		1	48.16	12.04
4	68.4363	1.3698	1.008	7.64		1	40.03	10.01

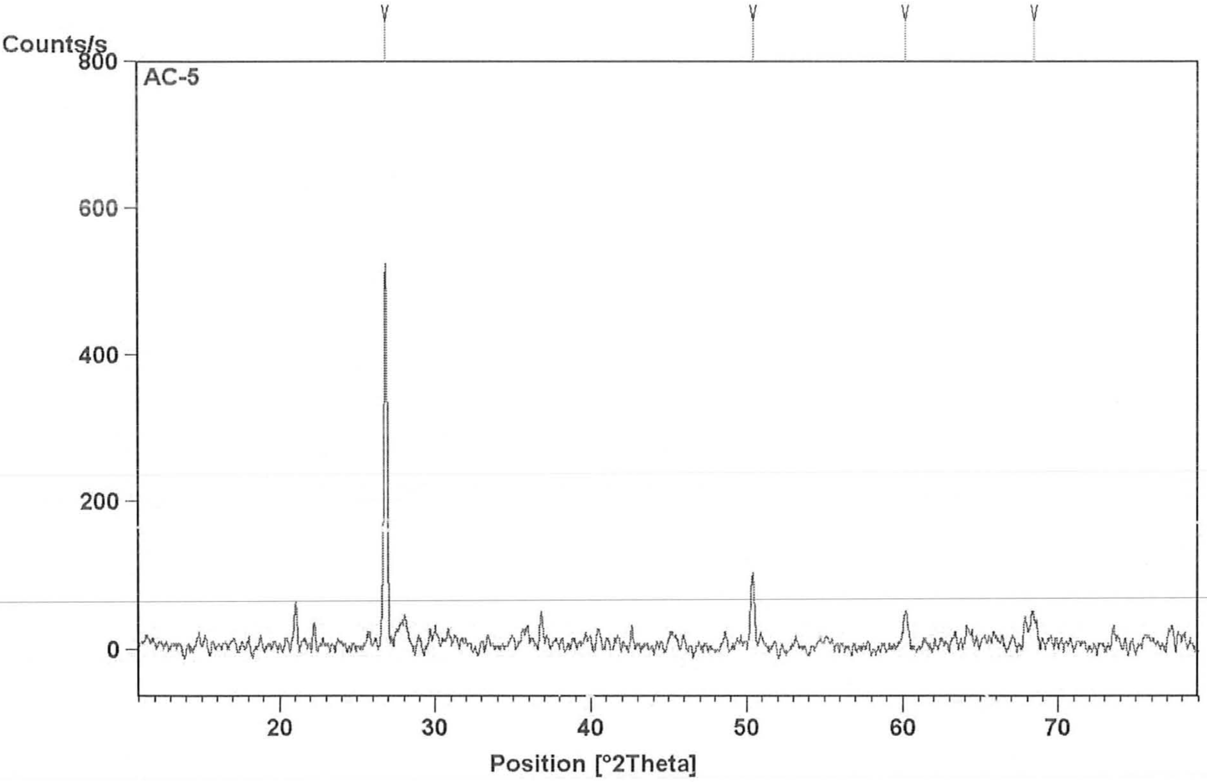

Figure 35: Morphology of the crystals present in the pottery power

The pottery that is obtained from all these sites has different chemical composition due to different crystalline structures as experimented through XRD. Therefore their provinence may be different. Pottery of each site is linked to the soil of specific area. The peaks are fingerprints of each crystal in the pottery. XRF only tells about the morphology of the crystals present in the pottery and it cannot tell composition.

CHAPTER 4

X-Radiography of Archaeological Metal Object of Buwagai, Chawgah, District Shangla

The chapter is divided into two parts. First part is an introduction to radiography and the second part is about the radiography of an archaeological metal object acquired from Buwagai, Chawgah, District Shangla, and Pakistan.

Part 1

X-Radiography

Archaeological investigations frequently yield numerous metal finds. These should be X-rayed as part of the post-excavation procedures to assist in the identification and interpretation of the finds, and thereby help understand the site. This procedure will also provide a record of the finds in the conditions in which they were recovered. X-radiograph itself provides a long-term visual record of inherently unstable and potentially deteriorating artefacts. While much can be done to slow down the deterioration processes of metal artefacts following their removal from burial, X-radiography should be initiated as soon after excavation as is practicable. A good quality X-radiograph may provide the information necessary to identify, classify, date and illustrate an object that has subsequently disintegrated beyond reconstruction. The benefits of X-radiography may be summarized as follows:

- Visual record of shape, technology and condition
- Aid to identification

- Non-interventive
- Non-destructive
- Cost-effective
- Long-term record of deteriorating objects (Jones 2006: 3).

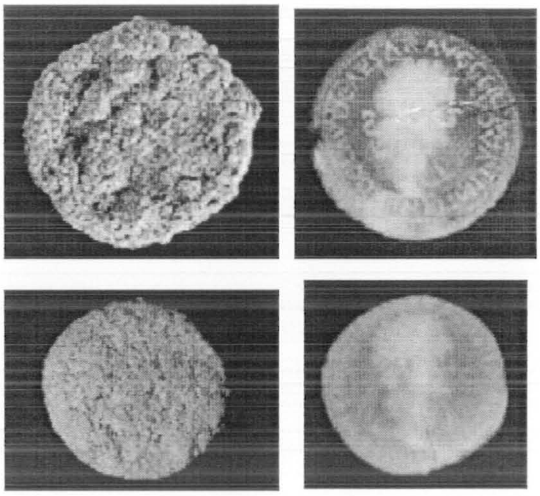

Figure 36: Coins can sometimes be dated from their X-radiographs. The two Roman coins, shown as excavated and their X-radiographs, are (upper) a sestertius of Nero dated AD 54–68 and (lower) a dupondius of Domitian dated AD 95–6 (Jones 2006: 3).

What X-radiography can Show

Object identification

Accretions can be so dense that the original shape of the object is obscured. This happens particularly with ferrous artefacts, which are more susceptible to this extensive form of deterioration A less-encrusted item might be readily identifiable when complete but subject to misidentification if broken and only partially surviving. Implements for writing, leatherworking and textile processing may be indistinguishable from broken nails when corroded, for example.

Similarly, coins with surface detail obscured by accretion can be identified by X-radiography in some instances. When this cannot be done, the radiograph informs decisions regarding the prioritizing of subsequent action (Jones 2006: 5).

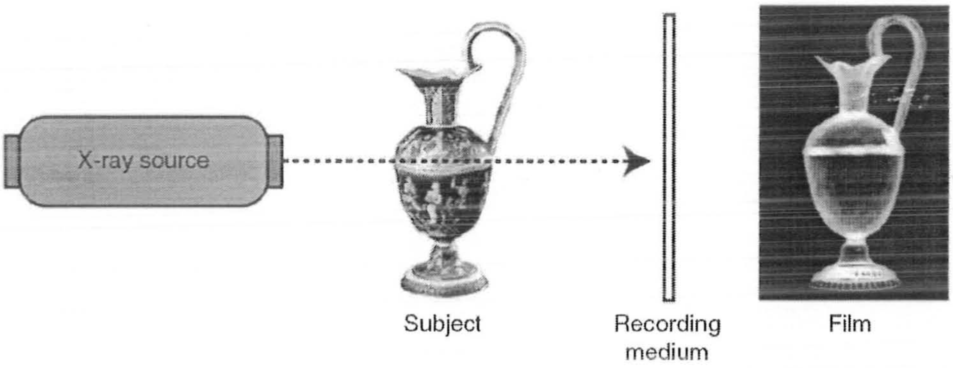

Figure 37: Process of X-Radiogrphy (Lang and Middleton 2005: 7)

Form and structure

X-rays will show size, shape and details of construction of the items under examination that will aid object identification as well as contribute to their characterization, technical description, classification and dating (Jones 2006: 7).

Surface features

X-radiography can elucidate decorative surface features – such as inlay, a wash of metal, or fields of enamel because the different chemical composition of the material comprising the object and that forming its surface decoration is revealed (Jones 2006: 7).

Technology

X-radiography can provide a range of technological information about the manufacture of an object, from details of the microstructure of the metals and alloys employed, whether it was made from sheet metal, wrought or cast, through to details of the construction of complex artefacts (Jones 2006: 7).

Condition

The archaeological interpretation of finds can depend on features of condition, such as completeness before burial or subsequent damage. Knowledge of the condition of an artefact, in terms of the presence of fissures, fractures or the extent of mineralization, can inform decisions on subsequent examination and the conservation program, particularly when finds are very fragile (Jones 2006: 10).

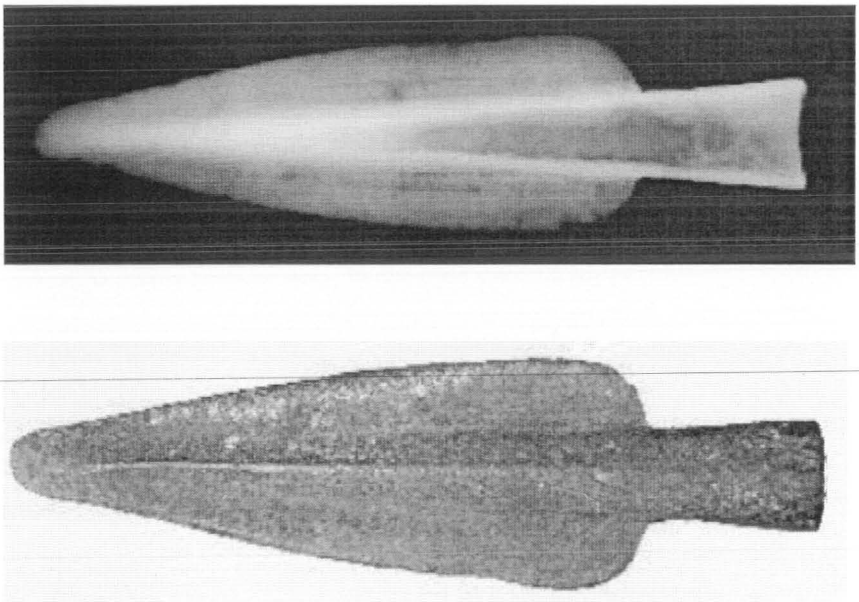

Figure 38: Medieval copper alloy spearhead. The X-radiograph shows complex structure within the blade, which is not visible on the object after conservation (Jones 2006: 7)

X-Radiography of Archaeological Metal Object of Buwagai, Chawgah, District Shangla

Metals are useful and versatile materials with both strength and ductility, and their exploitation has been a key element in the development of human material culture. As most metals are not immediately available but have to be extracted from their ores, their use implies a certain level of technical expertise, and recognition of technical advance is reflected in the use of the terms 'Bronze Age' and 'Iron Age' to describe the cultural horizons when these metals began to be used extensively. Metals can be formed into a desired shape by casting molten metal in a mould or by working solid metal with tools. Metals can be cut and joined, decorated by chasing or engraving and embellished by the addition of inlays, enamels and stones. The methods used to work the metal and fabricate objects reveal the particular skills of the craftsman and may also reflect the craft-cultural traditions of their society. Radiography has an invaluable role to play in the recognition of these techniques of manufacture and thus contributes to our knowledge of the societies that produced the artefacts, and to our broader understanding of the history of technology. The details of the construction of an object are not always immediately obvious: surface features and decoration may be concealed under layers of corrosion, joins might be internal and sometimes the signs of casting or working can only be found within the metal itself. Radiography can often be used to reveal these hidden clues to constructional techniques. However, it is frequently necessary to use information from other investigatory techniques as well. Examination at low magnification using an optical microscope may precede radiography, and chemical analysis is often necessary to confirm compositional differences indicated by the radiographic examination.

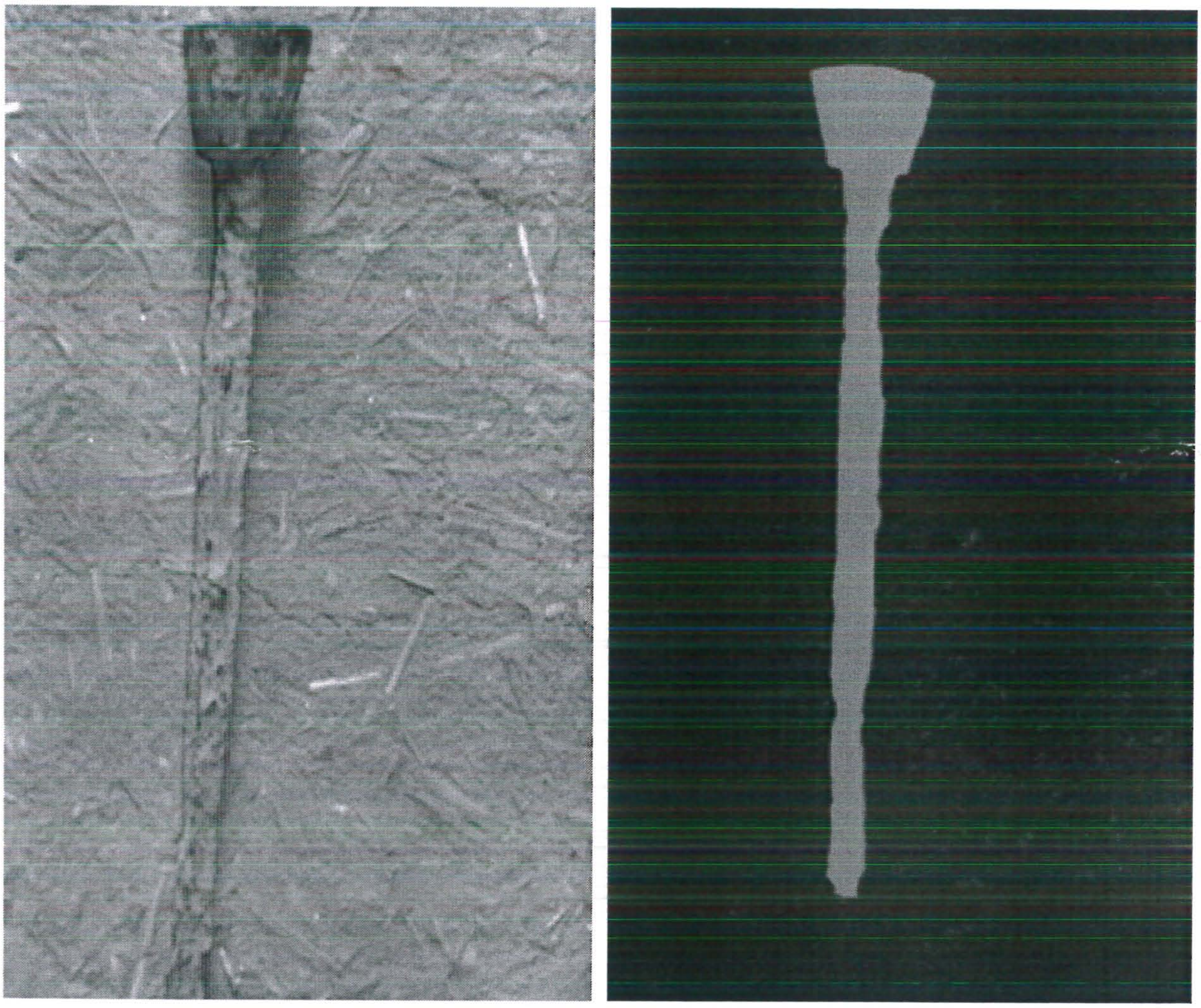

Figure 39: X-Radiography of Iron Nail (by the researcher)

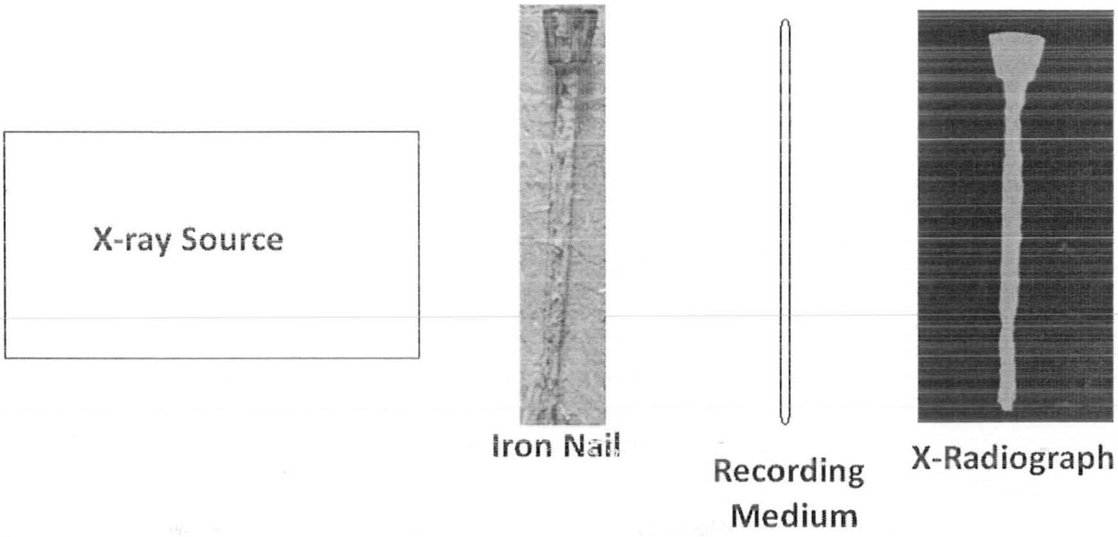

Figure 40: Scheme of X-Radiography (by the researcher)

The metal object acquired from the site is corroded. Its structure and shape is clear after X-Radiography. X-radiograph shows its boundary that is affected by corrosion. Similarly radiography for the examination of antiquities from the site is necessary. Application of X-Radiography can be used in the field of heritage conservation in Pakistan. It is at the initial stage of conservation that radiography, together with other scientific techniques, may be employed to supplement visual examination. It is an initial step toward advancement of archaeology in Pakistan. Useful information on both historical and archaeological objects is provided by radiographic examination therefore more work is to done on the archaeological materials found at the site. Other archaeological materials including ceramic, stone and items of organic origin, for example, wood, paper and human remains, can be radiographed as well.

Conclusion

Development in archaeological chemistry is simply revolutionizing archaeology. Applications of chemistry in archaeology are growing rapidly and definitely in the next 30 years there will be new developments and advancement in instrumentation like NAA, FTIR, GC/MS, EMPA, SEM, ESR, NMR, ICP-AES, LC/MS and many more for the analysis of a range of archaeological materials. In archaeology the extraordinary kinds of results can be achieved when several different methods of chemistry are applied. With the application of chemistry multiple kinds of evidences can be achieved from archaeology and that can provide greater insight or expose more information about the object or material under study. What will be the status of archaeological chemistry in the next decade or two in Pakistan and in the world? What new methods, instruments, and techniques will be used to understand ancient cultures? Archaeology in Pakistan has been treated very badly or archaeologists had no scientific knowledge in interpreting archaeological data therefore it can be predicted that there will be a revolution in Pakistan archaeology with new ideas and methods made by chemists. There will be more laboratories of archaeological chemistry in the future. Major scientific instruments are not available in Pakistan and maintenance and repair is a constant cost. Because of the costs, today there are relatively no laboratories in archaeological facilities. That situation will be improved when more academic departments add chemists to train archaeologists. Universities in Pakistan will have to find the higher levels of funding needed to build laboratories of archaeological chemistry. Students and professionals must be trained to understand and to carry out some of analyses themselves. Archaeology is moving toward the advance sciences. Archaeological chemistry is quickly becoming a large and important part of archaeology. The future for archaeological chemistry is very bright in Pakistan and in the world, as new methods and ideas will develop to improve understanding of the human past. The future of archaeology is in the laboratory. In addition archaeological students must be trained in archaeological chemistry.

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