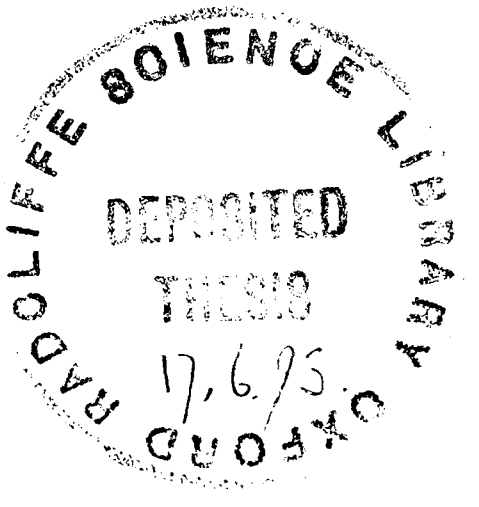
APPLICATION OF LEAD ISOTOPE ANALYSIS TO PROVENANCE STUDIES IN ARCHAEOLOGY.

Zofia Anna Stos-Gale

Christ Church
Michaelmas 1992

A thesis submitted in partial fulfilment
of the requirements for the
Degree of Doctor of Philosophy,
Department of Physics,
University of Oxford.



ACKNOWLEDGEMENTS AND THANKS.

I am very grateful to Professor K.W. Allen for most enlightening discussions, support and advice during the preparation of my thesis. I would like also to thank very warmly two other physicists: Dr. George Doucas of Oxford and Professor Al Silverman of Cornell for their sound scientific criticism, encouragement and advice. I am also grateful to all members of the Isotrace Laboratory for their cooperation and helpful atitude, and Martin Roberts for proof-reading and correcting the text. Finally I would like to thank my husband Noel Gale for introducing me to this fascinating subject and giving me the highest example of scientific discipline and hard work.

This work would not have been possible without the generous and continuous support to the Isotrace Laboratory from the Science Research Council, and to me personally from the Leverhulme Trust and the British Academy.

For Christopher

ABSTRACT.

Advances in mass spectrometry in the second half of this century allowed very accurate measurements of isotopic compositions of various elements. In turn it was discovered that due to the radiogenic origin of some of these isotopes their composition often reflects the geochemical history of minerals and rocks. Terrestrial lead is composed of four isotopes, of which three are radiogenic in origin as daughters of uranium and thorium. In geochronology the isotopic composition of minerals helps in dating the ore and rock formations. However, if there is enough diversity amongst the isotopic compositions of different deposits, then their lead isotope composition can be used as a simple and unique 'fingerprint', which can be scientifically measured. This feature can be used as a powerful tool in the identification of sources of ancient metals, because it passes unchanged through the smelting and refining processes. However, one of the most important requirements for such 'lead isotope provenance studies' is empirical investigation of the 'fingerprints' of ore deposits which are relevant to a given archaeological research. In this dissertation the scientific foundations of lead isotope provenance studies are described and examined in detail. All available evidence concerning the possibility of distinguishing isotopically between different European ore deposits is examined and methods of visual and numerical evaluation of the lead isotope data are suggested. Two examples of applications to specific archaeological problems are also given: the identification of sources of metals used for production of Bronze Age Cretan weapons and of non-ferrous metals in the Roman Period in Southern Poland. The interpretation of lead isotope data for archaeological objects is based on nearly 1500 isotopic analyses of ores.

CONTENTS.

1. INTRODUCTION.

In contrast with historical research, archaeology is mostly devoid of textual evidence; hence the reconstruction of the distant past is chiefly based on the examination of objects of material culture and other remains of life, such as bones, foodstuffs and architectural remains. Quite correctly therefore The Oxford Dictionary (1989) defines archaeology as "...the scientific study of the remains and monuments of the prehistoric period." In spite of the presence of the word "scientific" in this definition, archaeology is generally regarded as belonging to the humanities; only in recent decades have funds become available for an approach to this subject involving the natural sciences. At the same time, scientific and technological developments in physics and chemistry have greatly extended the range of methods of scientific examination which can be used to study archaeological objects. Different methods can provide information about the age of archaeological remains, their chemical composition, the technology of production, the geographical origin of raw materials, the identity of organic residues and plant remains, as well as the dietary habits of ancient people. During the past twenty years a new branch of science has developed: that of science-based archaeology or, as it is sometimes called, Archaeometry. The field is very varied and draws heavily on nuclear physics, organic and inorganic chemistry, biology, geology and geophysics. The biennial International Archaeometry Symposia present a cross-section of the scientific methods employed for solving archaeological problems (for example see 'Archaeophysika' 1978, Maniatis 1989, Pernicka and Wagner 1991).

Absolute dating information from archaeological or geological material is crucial for the chronological interpretation of our recent and more distant past; hence the C-14 and thermoluminescence dating techniques have already a firm position in archaeological research. Various methods of chemical analysis of ancient objects and remains are routinely used in research institutions and mu-

seums. However, perhaps the most interesting and promising breakthrough in science-based archaeology during the past ten years is the application of variations in the isotopic composition of elements such as Sr, O, N, C found in archaeological bones for the reconstruction of human diet, and elements like Pb, Nd, S, O, Sr for indication of the origin of raw materials used in prehistoric times. The materials studied by this new branch of scientific archaeology (perhaps, by analogy with Isotope Geology, we could call it Isotope Archaeology) include bones, pigments, glasses and glazes, metals, marble and ivory. The beginnings of Isotope Archaeology go back to the late nineteen-sixties when many scientific laboratories in the Western world were comparatively well funded and scientific research was conducted in a more relaxed manner. Many scientists were encouraged to try solving archaeological problems using scientific means and several archaeometric laboratories were founded. This development was strongly connected with the 'new wave' in archaeology itself. Modern archaeology is trying to read the past in a more historical way to discover the social and economic structures of the ancient societies, their diet, the development of technologies, trade contacts and sources of wealth. In all these areas, scientific methods of examination of the archaeological material, including isotopic and elemental analysis, are of great importance.

The identification of the sources of raw materials used and exploited by different peoples in different prehistoric periods is particularly important for the interpretation of ancient socio-economic structures and historical developments, since access to raw materials is crucial in the economy of any society or culture. The availability of metals such as copper, gold, silver and - since the Late Bronze Age - tin, very possibly shaped the politics and economies of Europe around the 3rd to 1st millenium BC. The base metals used at that time for tools and weapons were possibly as important for the development of wealth and power in Bronze Age society as is access to sources of energy in the second half of the

20th century. The politics of our world concentrate on geographical areas and countries rich in crude oil or uranium deposits. Some five thousand years ago stone and metals might have played a similar role for the ancient economy and politics. In some cases in the Bronze Age the shift in the centres of wealth and power might have been directly connected with working out small copper, silver or gold deposits, or perhaps with the development of new, more economical (i.e. larger, more accessible or containing more easily smelted ores) ore sources, or changes in, or access to, a particular trade route. To follow such patterns of change it would be most desirable to be able to study directly the sources of origin of particular goods and raw materials.

Another important factor in the reconstruction of the first societies is the development of technologies, particularly early metallurgy, which had an enormous impact on human history. Taking into account that Homo Erectus first appears on Earth some 1.5 million years ago, but the discovery of metal happened only some 7000 years ago, the acceleration of human progress in the age of metals is quite remarkable. Metals allowed better tools for building and agriculture; also better ships and carts could be made. This development facilitated better crops and food surplus, which created the potential for development of trade and art. To be able to reconstruct the trade contacts it is essential to establish the sources of raw materials and then to be able to trace their journey. For many early cultures there is no documentary evidence of trade; the only way to recognize the trade patterns is through the study of excavated materials.

In recent years, some progress has been made in the development of scientific methods of examination of archaeological objects to identify the origin of raw materials. Important advances have been made in identifying sources of obsidian, stone and pottery on the basis of their elemental composition and/or petrographic studies (Jones 1986). Attempts to discover the provenance of metals based on elemental composition failed, as might have been anticipated if

more thought had been given to the technology involved in production of metal from the ore. The elemental composition of metal produced during the process of smelting and refining changes so much, relative to that of the ore, that all attempts of this sort in linking a metal with the ore failed. However, the isotope measurements in provenance studies are much more powerful than the approach through chemical analyses. The variations in isotopic compositions of many natural materials reflect the geological history of a particular geographical area, providing a local scientific 'fingerprint'. More importantly, isotopic compositions are not susceptible to alterations during a pyrotechnological treatment, so that, for example, the lead isotope composition of a given metal ore remains unchanged in a metal object, mineral pigment or in the various by-products of metal smelting. In 1965, Brill suggested that lead isotope measurements of galenas and lead metal could link the two. In the late 1970s, Gale (1978) developed this technique and soon it was extended to silver, copper and iron. Various methods of isotopic fingerprinting of ancient materials are at present being developed in Oxford and Isotope Archaeology has a chance of becoming an important field of archaeological science (Stos-Gale 1992b).

At present, the Oxford Isotrace Laboratory is the only laboratory in the world applying thermal ionization mass spectrometry - TIMS (Chapter 3) - solely in research projects related to archaeology and the history of art. This thesis presents the recent advances and results in the application of lead isotope measurements to studies of the origin of metals. Lead isotope provenance research is a multidisciplinary field, where physics, chemistry, geology and archaeology play equal parts. It seemed helpful therefore to include in the first chapters of this work a short summary of the physics underlying the creation of isotopes (Chapter 2) and the technical aspects of measurements of lead isotopes (Chapter 3). The lead isotope provenance studies are based on the variations of the isotope composition of lead in different ore deposits, depending on the

geochemistry and the geological history of the deposit. These characteristic lead isotope compositions are called here the 'fingerprints' of particular ore deposits, and the identification of the origin of metal from which an object was made is based on the straightforward comparisons of these 'fingerprints' to that of an object. During the last few years (and as the experimental part of this thesis) we have accumulated several thousands of lead isotope data of the European copper and lead/silver ore deposits and archaeological metal artefacts. All data are stored in a computer data base which allows easy access for the interpretation of lead isotope data in the archaeological context. The work presented here is based on many years of experience in this subject and the largest data base available at present, which includes lead isotope, chemical, geological and archaeological data for each sample.

Several articles published in recent years created some confusion as to the possibilities and limitations of the lead isotope provenance studies. It seems that most of the published statements arise from a poor understanding of the physical and geochronological basis of this technique and the rather superficial nature of some projects (full discussion in Chapter 6). Outside Oxford the lead isotope data for the archaeological samples are obtained in geological laboratories, often without much understanding of the different requirements of archaeology as opposed to geochronology, and without an adequate data base. The lead isotope 'fingerprinting' of sources of materials used in ancient times presents problems distinctly different from those encountered in geochronology. For example, each lead isotope 'fingerprint' of an ore formation is a three-dimensional globule including a range of lead isotope ratios, rather than just one characteristic ratio. Therefore, establishing the 'fingerprints' of ore deposits requires a large number of analyses of different mineral samples (and the mineral should be relevant to the metal type of the objects) from one deposit to allow an estimate of the range of isotope compositions characteristic for that deposit. This aspect is hardly

ever important in geochronology where usually only three or four measurements are taken. On the other hand, because all the lead isotope provenance studies are based on experimentally established 'fingerprints' of ore deposits, all the geochronological models and theoretical problems encountered in the dating of geological formations are largely irrelevant to this work. It seems, however, that a better understanding of the method can be achieved with a short summary of the geochronological approach to lead isotope analysis (Chapter 4).

Much concern has been expressed recently in various publications as to the number of different ore deposits which might have identical or largely overlapping lead isotope compositions. It has been even suggested that lead isotope analysis, can only exclude, rather than assign, a number of ore deposits as a source of metal, because too many ore deposits are similar in their lead isotopic characteristics. The reliability, or otherwise, of the lead isotope method could be tested only by accumulating a sufficiently large body of experimental data. Therefore perhaps one of the most important parts of this work is presented in Chapter 6, where it is demonstrated for the first time that ore mineralizations have a strictly limited range of lead isotope compositions (the typical range is less than 0.5%) and that these compositions are, for the great majority of deposits relevant to the European archaeological material, sufficiently different from each other to provide a characteristic 'fingerprint' of the metal derived from this ore. Further, use of the multivariate discriminant analysis of lead isotope data can provide a quantitative estimate of the probability with which we can assign an archaeological object to a known ore deposit and make a quantitative distinction between ore samples from different geographical localities.

The second part of this work demonstrates the application of the lead isotope method to solving specific archaeological problems. The approach presented here is firmly based on geological and archaeometallurgical field work of the author, covering numerous lead/silver and copper deposits in the Mediter-

ranean and over a thousand lead isotope analyses of ores (Chapters 6 and 7). One of the most interesting aspects of the origin and development of the European metallurgy is presented by the metalwork excavated in Greece and dated to the third and second millenium BC. Crete in particular is known to be a centre of the earliest, exquisite metal work. The origin of the metal is a puzzle, because there is no direct archaeometallurgical evidence (mines, slag heaps, etc.) for exploitation of copper, lead or silver on Crete in prehistoric times. The lead isotope analyses of metal objects from Bronze Age (Minoan) sites on Crete and other archaeologically relevant locations provide a key answer to this question when compared to the lead isotope data of ores from the Aegean and the Middle East. The large number of analytical data available for this study allows a demonstration of the application of statistical methods of data analysis. The particular strength of the lead isotope analysis of metal artefacts lies in the fact that each object, independently of its state of preservation or lack of characteristic features (including lumps of metal, fragments of sheet metal *etc.*), can be associated with the place of origin of the mineral from which the metal was smelted. Thus a whole new pattern of the trade routes and economy of a given geographical region can be constructed. The Aegean archaeologists have already build up a most remarkable reconstruction of the movement of pottery in the Bronze Age. It is not possible, however, to proceed in a similar way (exclusively by studying the typology and manufacturing techniques) with metals. So far only the lead isotope 'fingerprints' allow identification of different origins of seemingly identical metal objects, or of metal scraps having no typology at all.

A quite different problem is presented by a group of much later metal objects from a site of the Roman period in South Poland (including alloys of copper with lead, zinc and tin, as well as some silver and lead metal) described in Chapter 8. The lead isotope analyses of these objects represent a small amount

of data for a group of metals from one site in a total 'analytical vacuum'. There has never been any lead isotope work performed on archaeological artefacts from this period and geographical area; only a few chemical analyses of similar metal objects have been published. There is no archaeometallurgical knowledge of the exploitation of metal deposits in this part of the world and only some lead isotope data for ore deposits have been published in geological publications. The accepted view of the origin of these metals is based mostly on Roman written sources and assumes that all the metal in *Barbaricum* was brought from the Roman Empire. In all probability, such metal was re-used many times and alloys were made repeatedly from scrap. Therefore, unless lead from another locality was added to the final alloy, the lead isotope 'fingerprint' of the metal should be entirely random. On the other hand, there still might be a possibility of drawing some conclusions from the lead isotope characteristics of a number of objects. There seems to be nothing known at present about the sources of metal in this part of Europe before the Middle Ages. Metal finds from Roman times in Poland are plentiful, however, and the confirmation of such considerable import from the Roman Empire would be an important addition to the knowledge of the relations between the Romans and the Barbarians. However, much closer than the Roman *limes* on the Rhine and the Danube are significant multimetallic ore deposits in Silesia, Saxony and Bohemia, and there are also records of the exploitation of gold, silver, copper and tin by the Celts. Is it really true that these metal ores were not used in earlier times, before their exploitation started in earnest in the Middle Ages? Lead isotope analyses can at least give an indication of the localities of sources of metals used in the Roman period site of Jakuszowice. The most important asset of lead isotope analysis in this part of the project is the possibility of finding the origin of metal from droplets of metal or shapeless scrap, which forms a considerable part of the excavated objects.

The subjects of isotope geochemistry, geology and science based archaeol-

ogy ultimately are based on physics and chemistry. Perhaps it might be worth while to start from the beginning...

A. THEORETICAL BACKGROUND
FOR LEAD ISOTOPE PROVENANCE STUDIES.

2. ELEMENTS AND ISOTOPES IN NATURE.

2.1. The origin of heavy elements and their abundance in the solar system.

Until the end of the 18th century, studies of the Bible provided an answer to the question of the age of the Earth: 4004 BC. From the 18th century onwards, other sources of information put this date in doubt: in particular, observations of the rates of sedimentation and erosion, together with the assessment of the amount of salt brought down by the rivers to the oceans, suggested dates much older, reaching millions of years. About a hundred years ago, Lord Rutherford for the first time put forward an argument for the time of the (assumed) fixed point in the past when the elements were created. The argument was based on the presence of still considerable quantities of long-lived radioactive isotopes naturally occurring in the solar system.

One of the more interesting questions related to the origins of our world is that of the time and mode of the creation of elements. It is now generally believed that the Universe was created about 15×10^9 years ago and at that time contained photons, neutrinos and antineutrinos, electrons and nucleons. The science of nucleogenesis attempts to answer the question of the origin of matter in whatever its primordial form may have been (Clayton 1968). The major advances in this field were achieved primarily in the nineteen-thirties when Eddington demonstrated that in stars energy can be transported from the centre to the surface by the process of radiative transfer. He developed in detail the corresponding theory relating energy flux to the temperature gradient. Around that time also Bethe and Weizsacker showed how hydrogen can be fused into

helium nuclei. Following that, Chandrasekhar (1939) published a discussion of thermonuclear reactions as the internal source of stellar energy. When stars form from gas in the interstellar medium they are primarily composed of hydrogen and helium. Those primary gaseous clouds are called protostars. Protostars contract gravitationally and heat up according to the *virial theorem* (Williams 1991) until the central temperature becomes sufficient to cause hydrogen thermonuclear reactions to begin, at which time they radiate energy at a rate equal to that liberated by the nuclear reactions in their interiors. As the hydrogen in the core is exhausted, the central region of the star becomes unable to generate sufficient pressure to support the overlying layers against gravitational contraction; they start to collapse and the star's temperature increases because of the gravitational work expended. This increase in central temperature, and therefore pressure, eventually causes the outer layers of the star to expand again to halt the temperature gradient. The gravitational contraction stops when the energy producing thermonuclear reactions starts to form helium nuclei. The helium is subsequently converted into carbon and oxygen in another reaction cycle. Eventually, a point will be reached when even the helium in the deep interior is also exhausted, and the star will undertake a further gravitational contraction and the products of helium will be heated towards a temperature at which they will interact. The nuclear reactions in the stellar interior probably account for the synthesis of most heavy elements. Chandrasekhar wrote in 1939 that: "... The transmutation of elements is the entire cause of the presence of all elements in the stars; they are all being synthesised continually in the stars which are assumed to have started as pure masses of hydrogen ...". More recently the background thermal radiation in the Universe was discovered; it is characterized by the $2.7^0 K$ black body spectrum, which was interpreted as the residue of a primordial fireball (Weinberg 1977). This primordial fireball might have produced many of the lightest elements, but further research shows that

the synthesis of heavy elements terminates with iron. However, heavier nuclei can be formed efficiently by the capture of free neutrons liberated as a by-product of reactions between light charged particles; a strong correlation has been established between heavy nuclear abundances and their neutron-capture characteristics.

2.2. Principles of nuclear decay.

If the known nuclei are arranged in the order of increasing Z and N, all isotones (that is nuclides of the same N) will appear in horizontal lines and all isotopes (having the same Z) in vertical lines (this is called the Segre chart). For small mass numbers, the stable nuclei cluster about the line N=Z=A/2, but the heavier nuclei (roughly above Z=25) have many excess neutrons. Some of those heavy elements are susceptible to natural radioactive decay through the emission of α particles (nuclei of ^4He), β particles (electrons) or γ (electromagnetic) radiation, producing in the case of α and β radiation isotopes of other elements. Radioactive decay takes place according to purely statistical laws. The constancy of the rate of decay of radioactive nuclei is expressed by the proportionality between the number of nuclei decaying in a given time interval and the total number of such nuclei existing at time t:

$$\frac{-dN}{dt} = \lambda N \tag{2.1}$$

where λ is the decay constant representing the probability per unit time of radioactive desintegration.

If there exist at time $t = 0$ a number (N_0) of radioactive parent atoms, then the number of radioactive parent atoms (N) that remain at any later time t is:

$$N = N_0 e^{-\lambda t} \tag{2.2}$$

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According to this law, the rate of accumulation ($\frac{dN}{dt}$)of daughter nuclei is fastest at time zero and becomes infinitely slow when the parent nuclei have almost completely disappeared.

At $t = 0$, that is at the beginning of the radioactive decay, the number of radioactive nuclei of a given isotope is N_0 and then the above equation leads to the age formula:

$$t = \frac{1}{\lambda} ln \frac{N_0}{N} \tag{2.3}$$

After a certain time the system will consist of M mother isotopes and D daughter isotopes which were formed during the time t (where $M+D = N_0, N = M$):

$$t = \frac{1}{\lambda} ln \left(1 + \frac{D}{M}\right) \tag{2.4}$$

This equation enables us to calculate the time which elapsed from the start of the radioactive decay to the present and forms the basis of many geological and archaeological dating techniques based on the radioactive decay of long-lived isotopes. The most common modes of radioactive decay are through the emission of α or β particles.

Radioactive decay is a nuclear process which progresses at a constant rate dependent only on the nuclear structure of the isotope and independently of chemical and physical conditions such as temperature, pressure, humidity and elemental composition. The rate of decay is characteristic for a particular isotope and can be defined in terms of a half-life or a mean life of the particular nucleus. The half life is the time required for one-half of a given initial number of radionuclide to decay, i.e.:

$$\frac{1}{2} N_0 = N_0 e^{-\lambda T_{\frac{1}{2}}} \tag{2.5}$$

therefore:

$$T_{\frac{1}{2}} = \frac{ln2}{\lambda} = \frac{0.693}{\lambda} \tag{2.6}$$

The mean life is defined as the average life expectancy of a radioactive atom:

$$\tau = -\frac{1}{N_0} \int_{t=0}^{t=\infty} t dN \tag{2.7}$$

The mean life is equal to the reciprocal of the decay constant:

$$\tau = \frac{1}{\lambda} \tag{2.8}$$

The discovery of the radioactivity of uranium and thorium at the beginning of this century was soon followed by attempts to measure the ages of uranium-bearing minerals. Three chains of decay of different isotopes of uranium and thorium produce as stable decay products three lead isotopes: for example each atom of ^{238}U ultimately produces one atom of ^{206}Pb by emission of eight α particles and six β particles. Similarly, the decay of ^{235}U gives rise to the actinium series which ends with stable isotope ^{207}Pb after emission of seven α and four β particles. The decay of ^{232}Th results in the emission of six α and four β particles leading to the formation of stable ^{208}Pb. Each of the lead isotopes formed in these decay chains occurs only in one of them (Figures 2 a, b, c).

The emission of α particles from heavy nuclei involves a transition from a state in which the particle is inside the nuclear potential to one in which it is outside the range of nuclear forces. The probability of this process, and therefore the lifetime of α decay, depends very strongly on the height of the potential barrier which the alpha particle must penetrate, and therefore on the nuclear radius R beyond which the repulsive Coulomb potential is not compensated by the attractive nuclear potential. All three parent isotopes of lead have very long half-lives in the range of 10^8 to 10^{10} years. The long half-lives of the isotopes

Fig. 2a. The decay chain of ^{238}U to ^{206}Pb.

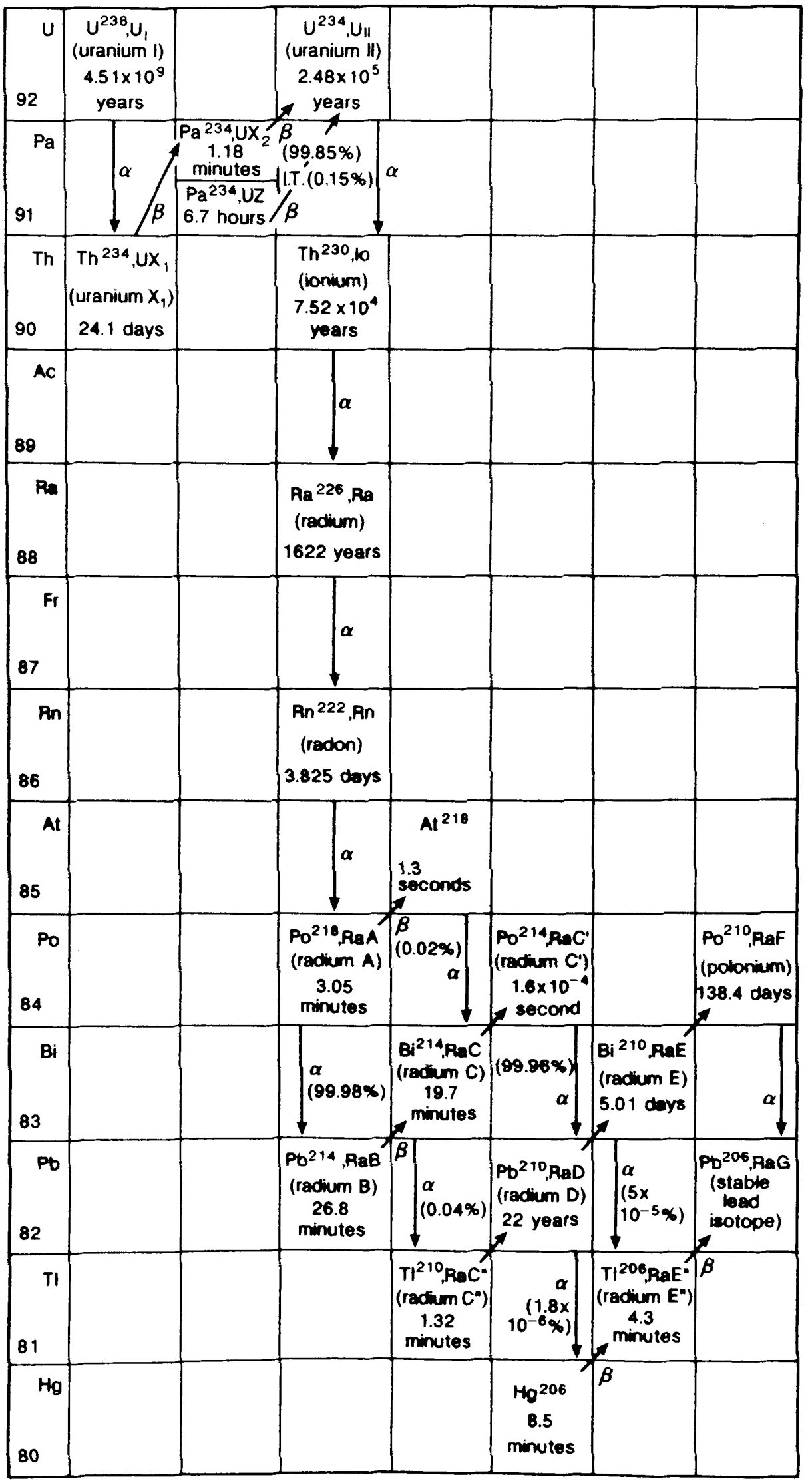


Fig. 2b. The decay chain of ^{235}U to ^{207}Pb.

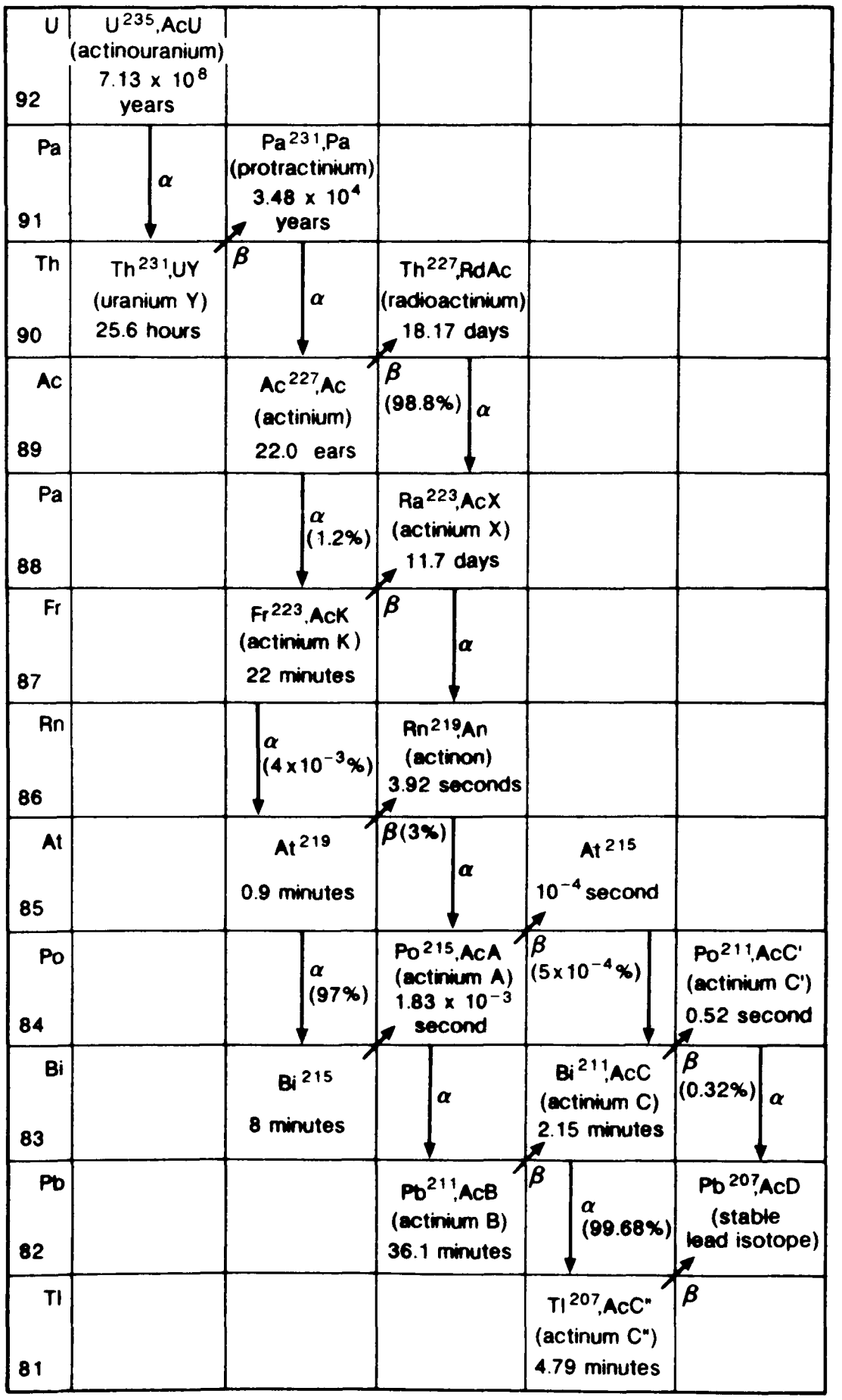
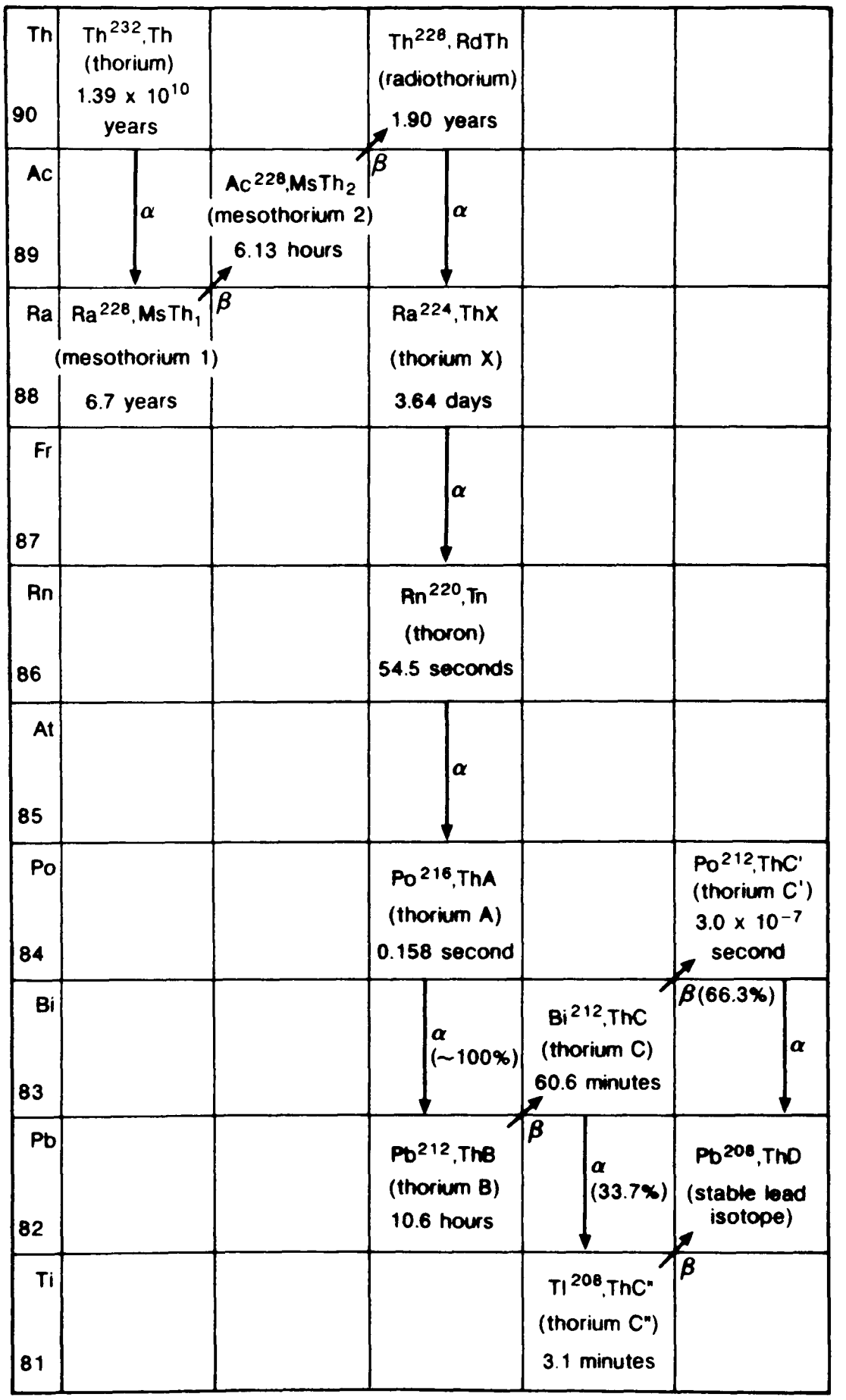


Fig. 2c. The decay chain of ^{232}Th to ^{208}Pb.



of the actinium series make them particularly suitable for dating of geological events and in the course of that their geochemical behaviour has been intensively studied in the last thirty years.

2.3. Isotope abundances of elements in the Earth's crust.

Much research time in this century has been devoted to measurements of isotopic abundances of naturally occurring isotopes of non-radiogenic origin (for references, see for example *International Journal of Pure and Applied Chemistry* **60 (6)**, 1988, 842-854). The *equilibrium isotope effect* is a physical phenomenon which causes the heavy isotope to accumulate in a particular chemical component of a system at equilibrium. The heavy isotope goes preferentially to the chemical compound in which the element is bound most strongly (Bigeleisen 1965). This effect can lead to *isotope fractionation*, that is enrichment or depletion of heavy isotope (Hayes 1982).

The research into *natural isotope fractionation*, that is a difference in isotope ratios of the same element in chemically different specimens, is carried out in many isotope laboratories and has principally two aims: one is to establish precise atomic weights of all elements and the other, applied mostly to meteoritic samples, is directed towards finding isotopic anomalies which might be significant in identifying a variety of astrophysical and cosmochemical phenomena. The classic picture of the pre-solar nebula as a hot, chemically and isotopically homogeneous cloud of matter has changed considerably over the past twenty years. A large number of isotopic anomalies have been discovered in a variety of meteoritic fragments and in terrestrial minerals. Natural isotopic fractionation is dependent on the relative mass difference between the isotopes, and therefore is likely to be more important in elements of low atomic number. There are, however, many processes of a geochemical, chemical or mechanical nature which can also produce isotopic fractionation of elements.

It has been established that fractionation between stable isotopes of the

light elements H, C, N, O and S is a consequence of many geological processes and has important petrogenetic applications in most branches of geochemistry. Some of the heavier elements also show natural fractionation of their stable isotopes, but of a lesser magnitude than the light elements. Such fractionations were observed in Ga (Gramlich and Machlan 1985), Pd (Mermelengas et al. 1981, Rosman and DeLaeter 1984), Te (Smithers and Krouse 1968, Smith and DeLaeter 1986) and Se (Krouse and Thode 1962). Another four elements, for which geological specimens are known in which the element has anomalous isotopic composition, are listed in updated tables of atomic mass of elements in the International Journal of Pure and Analytical Chemistry; they are Ba, Cd, Ce and Eu. However, all those reported anomalies are extremely small (in a range of 10^{-3}) and there is no geographical or mineral variation in these anomalies. Also there are no physical or chemical bases for their explanation. At present it seems that they are just random small isotope fractionations of unknown character. Pd isotopic anomaly in one mineral sample was confirmed by two independent teams, but no fractionations of Pd isotopes were found in any other minerals (Rosman and DeLaeter 1988). Clearly, some of the other isotope anomalies must be confirmed by repeated measurements before any further research can be based on them. Additionally, the majority of these elements does not appear in common archaeological materials in sufficient amounts to be of interest for the Isotope Archaeology.

It seems that at present only isotopic differences originating from spontaneous radioactive decay of elements found commonly in great abundance in nature provide a soundly based scientific tool for linking ancient objects with the sources of raw materials.

2.4. Isotope fractionation of tin and copper.

Two elements which are of a particular interest in the research into the origin of metals in antiquity are copper and tin. They are two major compo-

nents of the earliest metal produced by European man. The origin of tin in the earliest Mediterranean bronzes is of great interest, because this part of the world is practically void of tin occurrences, whilst tin is abundant in bronze artefacts. The nearest occurrences of cassiterite, which might have been used in the Bronze Age Mediterranean, are in central Europe, Spain, Cornwall and perhaps in southern Turkey. The other possibilities of sources of tin for the Bronze Age Mediterranean people are in Asia and the far East, where the largest tin deposits in the world are situated. Presently, south-east Asia, South America, Australia and Africa control 80% of the world's supply of tin. The possibility of tracing isotopically the origin of tin used in Europe in the third millenium B.C. is very tempting.

During the last thirty years, De Laeter and his colleagues at Curtin University (Perth) conducted many experiments to establish tin isotope fractionation in terrestrial cassiterites in connection with measurements of the atomic weight of this element (De Laeter and Jeffery 1965 and 1967, De Laeter et al. 1974, Rosman et al. 1984, Rosman and McNaughton 1987, McNaughton and Rosman 1991). In their latest paper, McNaughton and Rosman (1991) concluded that : "Terrestrial cassiterite Sn for the most part is unfractionated ... which must ultimately reflect the high efficiency of Sn dissolution and precipitation processes in the geological environment ... natural Sn fractionation is not common and not large, as first indicated by De Laeter and Jeffrey." Therefore, for the moment, tin isotopes do not seem a hopeful prospect for providing answers to some of the most interesting archaeological questions.

Another metal which greatly influenced the development of European civilization is copper. The first metal tools in Europe were made from copper and its improved variety: arsenical copper. The availability of metal tools changed the character of society, allowing more efficient farming and hunting, shipbuilding and domestic tasks. Finding the sources of this metal and the trade routes

would give valuable information about the economical structure of Europe at the dawn of civilization.

Natural variation of copper isotopes has not been investigated as thoroughly as that of tin. The only wide-ranging research into this subject was carried out in the US National Bureau of Standards many years ago (Shields et al. 1965). Shields and his colleagues analysed 106 samples of different copper minerals from various localities and came to the conclusion that there is a measurable isotopic variability in copper minerals. However, on the bases of the selected specimens it seems that the variability depends on the type of mineral rather than on its geographical origin. We have suggested using lead isotopes for fingerprinting of copper metal and copper ores (Gale and Stos-Gale 1982). This approach works quite well, but it would be a great step forward if copper isotopes could be used as a second type of isotopic signature.

3. PRINCIPLES OF ISOTOPE MEASUREMENTS.

3.1. Mass analysis.

The first measurements of atomic masses were performed at the beginning of this century by J.J. Thomson, Dempster and Aston. The principle of the measurement is very simple: charged particles (ions) are accelerated in vacuum by a high voltage and then they enter a magnetic field. If the magnetic field is perpendicular to the velocity vector of the ions, then the radius of the circular trajectory of the ions depends on their momentum:

$$Br = \frac{P}{e} = \frac{\sqrt{2mE}}{e} \tag{3.1}$$

where B represents the strength (magnetic induction) of the magnetic field, r is the radius of the trajectory, m is the mass of the ion, E is the energy, P the momentum and e is the electric charge of the ions; if e, B and E are constant then for larger m_e the radius r grows larger. For singly charged ions accelerated through a potential V to a velocity v, $P = mv$ and $E = \frac{1}{2}mv^2 = eV$.

Most modern mass spectrometers are based on the design introduced by Nier in 1940 where the deflection of the beam takes place in a wedge shaped magnetic field.

The instruments designed for measurements of atomic masses or isotopic compositions are called mass spectrometers (in older literature the name 'mass spectrograph' stands for an instrument in which ions are detected photographically). Amongst such modern mass spectrometers there is a broad trichotomy of types. The instruments used for measuring isotope ratios can be divided into solid source thermal ionization, gas source and accelerator mass spectrometers. Gas source mass spectrometers are used for all elements which can conveniently be converted to gaseous form (principally N, O, S and C). For heavier elements (above Li) the most accurate method of measurement of isotope ratios is ther-

mal ionization mass spectrometry. A single stage Nier-type mass spectrometer consists of three parts (Fig.3): a source of positively charged mono-energetic beam of ions (S), a magnetic analyzer (M) and ion collectors (C). The magnetic analyzer and the collectors are at all times in vacuum (less than 10^{-8} torr); the source is evacuated before each run and diferentially pumped.

3.2. Thermal ionization mass spectrometers.

A. Thermal ionization.

So far the only technique capable of sufficient accuracy both for isotope geochemistry and for archaeological applications is solid source thermal ionization mass spectrometry (TIMS), using mass spectrometers of the magnetic sector type. The thermal ionization technique, used by Dempster (1918) in his original mass spectrograph, depends on the fact that when an atom or molecule evaporates from a heated surface, there is a probability that it will evaporate as a positive ion. This can occur if the metal surface has a higher affinity for retaining an orbital electron from an escaping atom than does the atom itself. The efficiency of the ionization process has been shown theoretically to be governed by the Langmuir and Kingdom (1925) equation:

$$\frac{n^+}{n^o} = exp\frac{W-I}{kT} \tag{3.2}$$

where:

n^+ - number of positive ions

n^o - number of neutral particles

W - work function of the surface [eV]

I - ionization potential of the constituent evaporated [eV]

$$1eV = 1.6021917 \times 10^{-19} J$$

k - Boltzmann's constant ($1.380662 \times 10^{-23} JK^{-1}$)

T - filament temperature in ^oK

In order to achieve high ionization efficiency the work function of the ionising surface must be high and the ionization potential of the material to be analysed must be low.

Table 1. Electron work functions and melting points of filament materials used in TIMS.

Filament material	**Melting point (^oC)**	**Work function W (eV)**
Platinum - Pt	1772	5.13
Tantalum - Ta	2996	4.30
Rhenium - Re	3180	4.98
Tungsten - W	3410	4.58

For the most effective ionization, a salt of the element is deposited on an outgassed metal ribbon (filament) with high electron work function. The compound on the filament must be in a refractory form in order to prevent evaporation before ionization takes place at high temperature. Ta, W, Re and Pt have high work functions but zone refined rhenium is most often used because of its high work function and high melting point (3180^oC). The filament is heated by passing through it a highly stabilized electric current. Table 1 (adapted from Heumann 1986) gives the work functions of metals used most often for TIMS.

The ionization efficiency for different elements can be improved by loading them on the filament in a solution mixed with an activator (usually silica gel and phosphoric acid) or moderator (graphite). For example uranium ionization efficiency can be increased by two orders of magnitude by using the graphite 'sandwich' technique (Arden and Gale 1974, Chen and Wasserburg 1981). The actual mechanism of the graphite surface modifier is not well known, but it shows the following advantages:

1. It helps to attach the salt to the filament and acts as a reducing agent; it reduces emission of UO, so that U remains on the filament at temperatures up to 1950^oC, thus improving ionization efficiency.
2. Refractory U compounds, such as UC_2, are formed on the filament; when ionized, the major ionic species is U^+ and only small fractions of UC_2^+ or UO_2^+ are observed.

For lead isotope mass spectrometry by far the most common arrangement used for production of positive ions from a solid sample employs a single heated ribbon filament of rhenium on which the sample is placed, with an activator of silica gel and phosphoric acid (Cameron et al. 1969), though where large enough samples are available a more accurate triple filament technique is used (Catanzaro 1968; Elliott 1963).

The use of standards for calibration of the instrument allows the measurement of 'absolute ratios'. The US National Bureau of Standards provides isotope standards for most of the elements commonly analysed by mass spectrometry.

B. The source.

The ion source of a thermal ionization mass spectrometer consists of a metal filament with a sample of the element to be analysed mounted on a block which is placed in front of a series of focussing slits. The aim of the ion source is to produce and accelerate as many ions as possible into a narrow beam. The slits operate at high voltage optimized to obtain a maximum emergent ion beam intensity. The ions are accelerated to a moderately high voltage (6-10 kV) and collimated by a system of slits.

In the majority of ion sources both positive and negative ions will be formed during the heating of the filament. Most elements, however produce positive ions in much greater numbers hence the standard machines are build for the measurement of positive ions. Recently there have been developed special techniques for negative thermal ionisation mass spectrometry to extend TIMS to elements

such as Cl, B, Tc, Pt, Os (Wachsmann and Heumann 1991), but this will not be further considered here.

C. Mass analysis.

The mass analyzer usually consists of an electromagnet which separates the single beam emerging from the source slit into several beams of different mass/charge ratio. The beam travels in a curved evacuated tube consisting of highly polished stainless steel or glass (internally coated to be conductive) and is placed between the pole pieces of the electromagnet. Modern mass spectrometers usually have a 60^o to 90^o magnetic sector field with a 23 to 50 cm principal radius. This type of magnetic analyser provides direction focussing (as illustrated on Fig. 3), but no velocity focussing. This is not a problem if the ions are produced by thermal ionisations, since this process produces ions which are nearly mono-energetic (c. $0.2eV$ energy spread).

With the symbols used in section 3.1. the fundamental mass spectrometer equation can be re-written as:

$$r = \frac{1}{B}\frac{\sqrt{2mV}}{e} \tag{3.3}$$

which shows that successive $\frac{m}{e}$ groups can be brought into focus at the collector slit (C) by varying either V (the source accelerating potential) or B (the magnetic field). If ions of different mass have the same charge e, then this procedure yields mass analysis. At energies of the order of 10 KeV, all ions are singly charged.

Differentiating Equation (3.3) with B constant gives the dependance of the deflection of the ion beam on the stability of high voltage V as:

$$\frac{\Delta r}{r} = \frac{1}{2}\frac{\Delta V}{V} \tag{3.4}$$

Similarly the dependance on the stability of the magnetic field can be shown to be governed by:

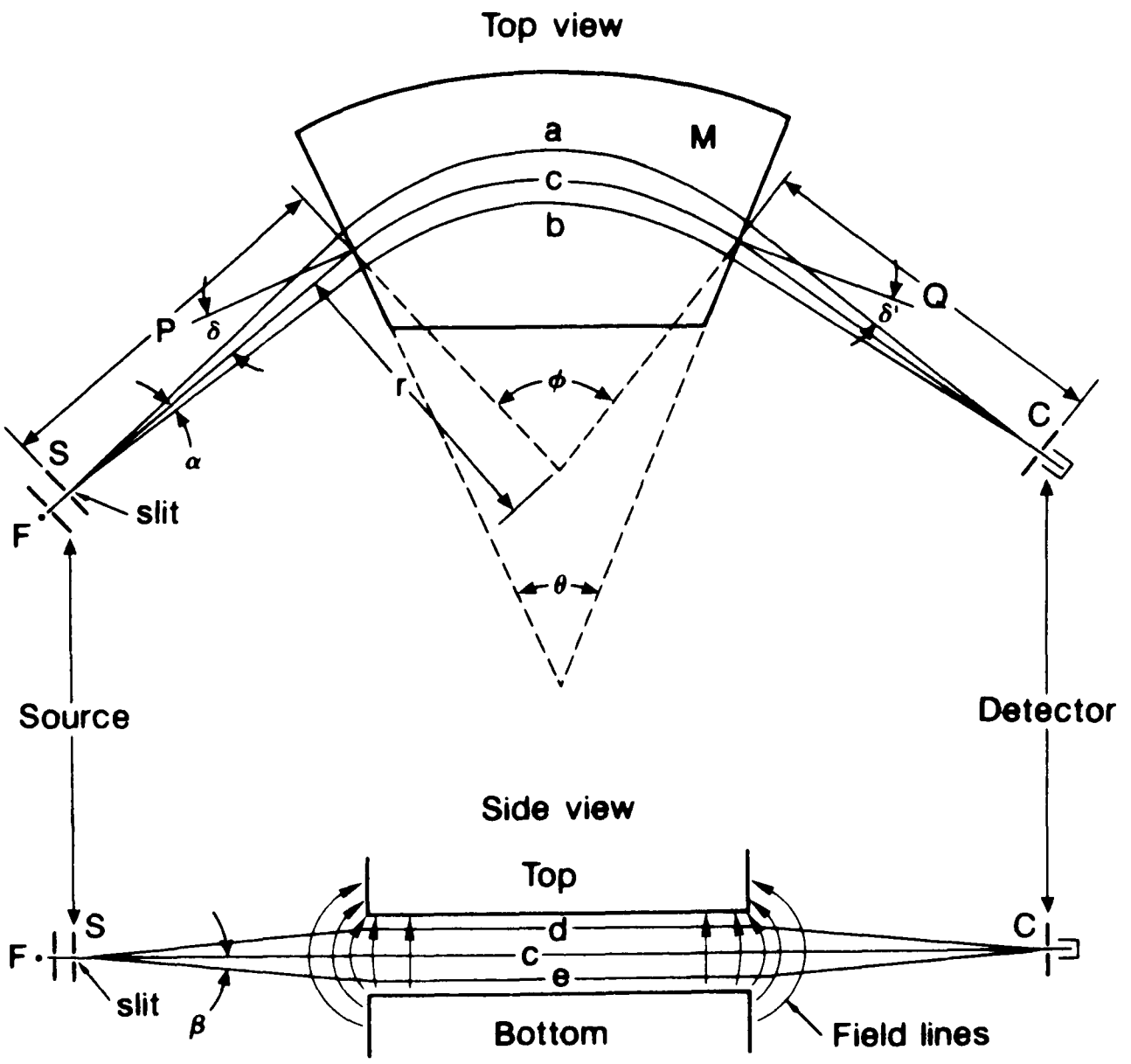


Fig. 3. Graphic representation of the first order direction focussing in the magnetic analyzer of a mass spectrometer.

$$\frac{\Delta r}{r} = \frac{\Delta B}{B} \tag{3.5}$$

These two equations indicate that the ion beam deflection is twice as sensitive to change in the magnetic field than it is to a change in the source accelerating voltage.

Figure 4 shows the mass spectrum formed by scanning ion beams across a collector slit. The beam enters the slit at point A, at the point B is fully inside the slit and at the point C it is leaving the slit. In this spectrum the width of the peak top is equal to $W_c - W_b$, the width of the peak bottom is equal to $W_c + W_b$, and the width of the peak shoulders is equal to the beam width W_b.

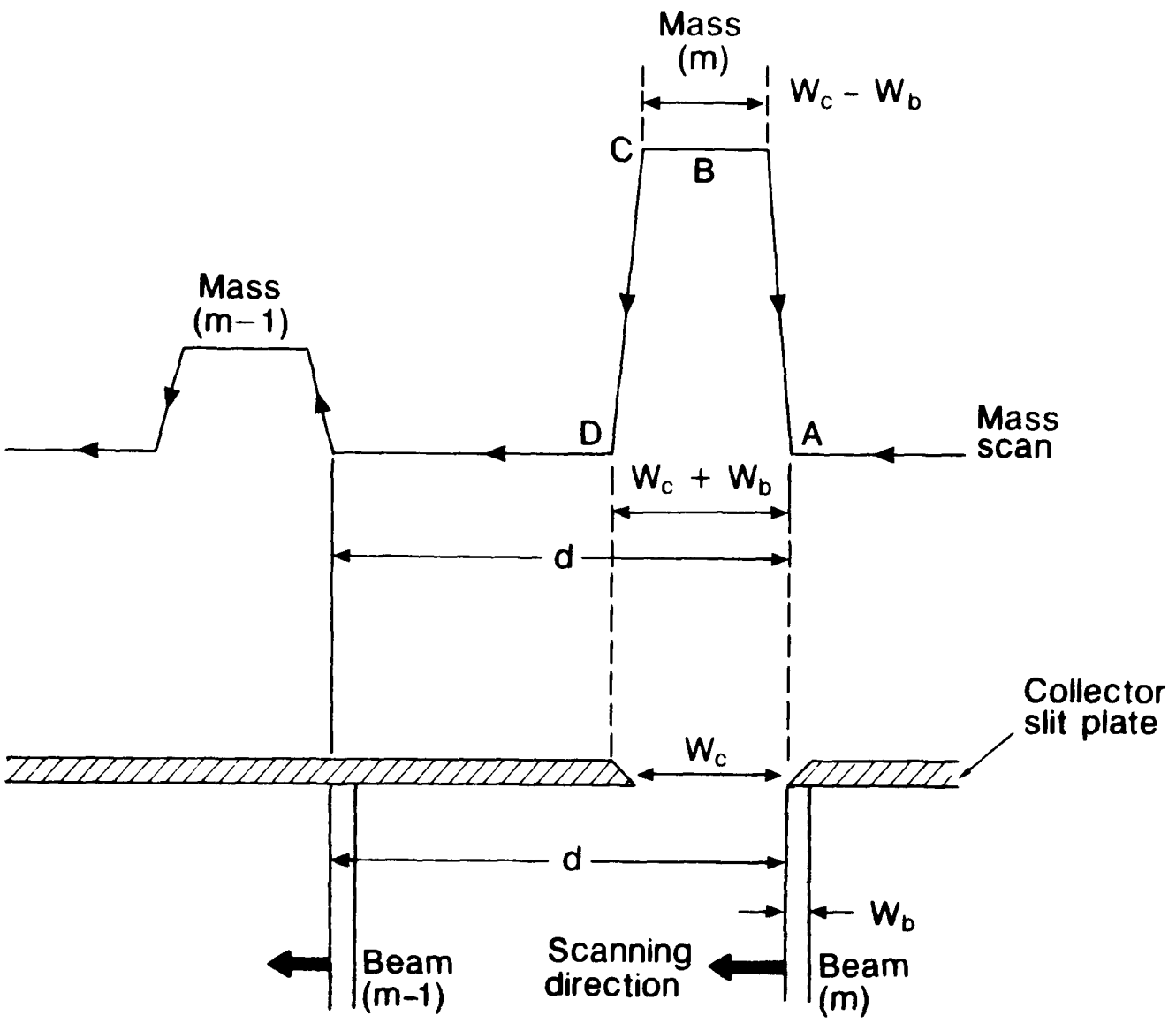


Fig. 4. Two peaks of mass m and $(m-1)$ formed by scanning ion beams across a collector slit.

W_c is the width of the collector slit.

The case illustrated is for a well-focussed beam (sharp ion image) and appropriately chosen defining slits and instrument resolution, so that flat-topped peaks are produced (with heights strictly proportional to the beam intensities), with well-defined valleys between peaks. These are the design criteria for a mass spectrometer intended for precise determination of isotopic compositions.

It is clearly important that the peaks for two adjacent masses do not run into each other, i.e. that they are well resolved from each other. This requires that the dispersion d (see Figure 4) at the collector slit, that is the distance between two adjacent peaks, is sufficiently large. In practice:

$$d = D\frac{\Delta m}{M} \tag{3.6}$$

where Δm is the mass difference between two ion beams, M is their mean mass, and D is defined as the dispersion length. D is a function of the radius of the magnetic field; for a symmetric 90^o sector magnet of radius R, with pole angles normal to the ion beam direction $D = R$.

For the idealised trapezoidal peak shapes of Figure 4 we can define a theoretical resolution (resolving power) in terms of the maximum mass number when two adjacent peaks are just resolved, that is, their bases just touch. Defining resolution R as $\frac{m}{\Delta m}$ for this situation, it follows from Figure 4 and Equation (3.6) that:

$$R = \frac{M}{\Delta m} = \frac{D}{W_c + W_b} \approx \frac{D}{W_s + W_c} \tag{3.7}$$

where W_s is the width of the source slit (in practice $W_b \approx W_s$), W_c is the width of collector slit and D is the dispersion length.

In practice the ion image is often diffused at the edges, so that the peaks do not terminate abruptly, but tail into the base line. In this case Δm, the peak width, is taken at an arbitrary 10% of the full peak height and the resolving power is said to be at the 10% valley level. Equation (3.7) shows that the resolution $\frac{M}{\Delta m}$ increases with increasing radius of curvature (since $D \simeq R$) of the magnet or decreasing slit widths (which will tend to reduce transmission of the instrument).

D. Ion counting system.

Measurement of ion currents down to 10^{-12}A usually makes use of a Faraday cup and a vibrating reed (capacitor) electrometer amplifier. Use of a Daly detector (Daly 1960) or an electron multiplier potentially can increase ion detection sensitivity by a factor of at least 10^4, though for precise measurements

such detectors are usually used (in the analogue mode) to provide a gain of 20 to 100 relative to a Faraday cup system. There are considerable technical advantages if the Daly detector is used in an ion counting, rather than analogue, mode (Turner 1988).

The Faraday cup (or a Daly detector) is located just behind the collector slit at the focal point and accepts only one of the separated ion beams at a time. Using a Faraday cup (or multiplier in analogue mode) the intensity of each beam is measured by the charge from the ions to flow through a very high resistance (10^9 to 10^{12} ohms). The resulting potential difference across the resistor is proportional to the intensity of the incident ion beam. The total charge Q after a period of time t is:

$$Q = net \tag{3.8}$$

where n is is the frequency of ions (ions/sec).

The ion current is given by $I = \frac{dQ}{dt} = ne$. The voltage across the resistor is equal to $V = iR = neR$.

Using a Daly detector in ion counting mode, for which the background can be below 0.1 cps, it is practicable to make ion current measurements down to 10 ions per second (a current of 1.6×10^{-18} A) and (limited by deadtimes of the order of 10 nanoseconds) up to about 3×10^6 ions per second (about 5×10^{-13} A). The Daly detector converts ions to electrons (on an aluminised knob held at about -30 kV) which are detected by a fast plastic scintillator viewed by a fast photomultiplier. The detection of electrons obviates the damage to the scintillator which would be caused by direct detection of positive ions (Daly 1960).

Most thermal ionization mass spectrometers built in the last five years have multiple collector systems. In such machines a number of Faraday collectors (usually six or seven) are spaced along the line of focal points. With the

appropriate settings for different masses, several ion beams are detected simultaneously. The beams can be measured in a static mode, where each beam is counted in the same collector throughout the run, or in a dynamic mode, where the beams of ions of a given mass for each block of data are counted on a different collector, so eliminating effects due to different collector efficiencies. The multicollector system provides much better precision of measurements, because the fluctuation in beam intensity is averaged out very effectively.

3.3. Instrumental mass fractionation and accuracy in thermal ionization.

In Chapter 2.4. *natural isotope fractionation* was mentioned and defined as different isotope abundances in different specimens of the same element. Another type of isotope fractionation is that of *instrumental isotope fractionation* which causes the observed isotope ratios in a thermal ionization mass spectrometer to be different form the true isotopic composition of the sample. The observed isotope ratios depend on the time when they were measured during the run (due to the different rates of evaporation of ions of different masses), on the chemical form of the sample, the temperature and the material used for the ionization filament. Therefore, the accuracy of determination of lead isotope abundance ratios using the thermal ionization method is limited by variable mass fractionation (Elliott 1963) in the mass spectrometer. Moreover, the specific procedure chosen for loading the sample on the filament and the preheating procedures also might influence the observed ratios. All those factors make impossible the direct comparison of experimental results which have been obtained by different laboratories. To overcome these difficulties all laboratories correct measured isotope ratios for instrumental fractionation effects.

For some elements corrections can be applied for variable mass fractionation during mass spectrometry in terms of an inherent isotope ratio which is naturally constant. This procedure is called *normalization to an internal stan-*

dard. For example natural strontium is composed of four isotopes of atomic mass 88, 87, 86 and 84. Only ^{87}Sr varies in abundance in nature, due to augmentation by the decay of naturally radioactive ^{87}Rb; the other isotopes of strontium are not fractionated by geological processes. Very accurate measurements of the ratios $^{87}Sr/^{86}Sr$ and $^{84}Sr/^{88}Sr$ can be made by normalizing to the constant ratio $^{86}Sr/^{88}Sr = 0.1194$; in practice $^{87}Sr/^{86}Sr$ ratios can routinely be measured to an accuracy of $\pm 0.01\%$ ($2\ \sigma$ level). This technique can be applied also to other elements such as Nd and U.

This approach is not directly available for determination of many other isotopes, and in particular for the three isotope ratios of lead, since all three ratios vary in nature due to augmentation from the decay of the naturally radioactive isotopes ^{238}U,^{235}U and ^{232}Th.

Tuttas and Habfast (1988) listed several factors which are important to keep instrumental isotope fractionation to a minimum:

1. The sample size must be sufficient for the completion of isotope ratio measurements using only a small fraction of the whole sample. It is best to avoid measurement of isotope ratios of the layers of sample directly adhering to the filament, where chemical changes might have taken place. In this way the differential mass dependant evaporation processes are minimised.
2. The molecular weight of the sample should be as high as possible, in order to have the relative mass difference of the evaporating isotopic species as small as possible.
3. Samples used in isotopic analyses should be as chemically pure as possible to prevent any significant interference from different molecules.
4. The sample should be loaded in such form that only one chemical species will evaporate.

With the lead sulphide or lead nitrate technique in general use for thermal ionization mass spectrometry (TIMS) in the nineteen-sixties the minimum

sample size was about 1 microgram of lead and the absolute 2σ errors in the isotope ratios were about $\pm 1\%$ or larger. In 1968 Catanzaro et al. published a triple Pt filament TIMS technique which allowed lead isotope ratios to be measured to about $\pm 0.05\%$ at the 95% confidence level, but the technique required 1000 microgram samples, too high for most archaeological (or geological) applications. This did however allow the United States National Bureau of Standards (NBS, now NIST) to prepare and certify three international lead isotope reference standards, so that henceforward all laboratories could place their lead isotope analyses on an absolute basis using the *normalization to an external standard.*

The next advance was the independent investigation of the use of emitters, which not only greatly increased the sensitivity of the thermal ionization method for lead isotope analysis but also improved the accuracy by an order of magnitude. In 1969 Cameron et al. published a technique using a silica gel emitter which allowed of the order of 300 nanograms of lead to be isotopically analysed. In fact Akishin et al. (1957) in Russia had published a similar technique a decade earlier, and Amov (1968) in Bulgaria also anticipated the American work, but these developments took a long time to become widely known in the west. It was however not until 1973 that Barnes and his colleagues at the National Bureau of Standards in the USA, and independently Arden and Gale (1974) in Oxford, published low blank (blanks of about 1 nanogram Pb) chemical separative techniques for lead and a silica gel emitter technique which allowed 100 nanogram samples of lead to be measured to better than $\pm 0.1\%$ (at the 95% confidence level). Both isotope geochemists and archaeometrists have almost universally adopted the silica-gel emitter technique to produce lead ions for mass analysis. A maximum of $1\mu g$ of lead in solution, usually as the nitrate, is placed on a thin substrate of silica gel with a small amount of phosphoric acid on a rhenium metal ribbon filament. Lead ions are produced by heating

this filament to $1100 - 1200^{o}C$. This technique routinely produces ion beams of the order of $5 \times 10^{-11}A$ and within-run precision of the order of 0.005% for the ratios $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ and 0.02% for the $^{206}Pb/^{204}Pb$ ratio (at the two sigma level). However, according to the exact details of the technique used, most laboratories experience inter-run mass dependent isotopic fractionation, which requires application of a correction factor of the order of 1.0014 per atomic mass unit difference between the two isotopes which comprise a measured ratio (see Appendix 1). As explained above, this is corrected in terms of measurements under the same conditions of the NBS lead isotopic standards SRM981 or SRM982. The net effect is that the absolute accuracy of modern lead isotope ratios is about $\pm 0.05\%$ for $^{207}Pb/^{206}Pb$ and $\leq \pm 0.1\%$ for $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ ratios.

Another influence on the observed isotope ratios is fractionation with time. Several different numerical methods of fractionation corrections were suggested in recent years (Tuttas and Habfast 1988) and the accuracy of thermal ionization measurements can be greatly improved by applying different fractionation models to correct the data. However, many phenomena encountered in the thermal ionization process are still unexplained and "... some appear to verge on black magic ..." (Tuttas and Habfast 1988).

Unfortunately all these problems with the accuracy of measurements of lead isotope ratios greatly limit the utility of all archaeometric and most geological lead isotope work reported up to about 1974. This problem is particularly apparent in archaeological provenance studies, where (as will be demonstrated in following chapters) different ore sources must be very accurately defined isotopically. The whole range of lead isotope compositions found in ore deposits is only about 8%, whilst most fall in a region covering a range of about only 1.7%. To be able effectively to discriminate between the lead isotope compositions of ore sources it is necessary to be able to determine lead isotope ratios with ac-

curacy of less than or equal to about ±0.1% at least. Since almost all of the earliest work in the field of archaeological lead isotope provenance studies published by Brill involved analyses made for him at NBS (using the lead sulphide method), all of Brill's analyses published prior to 1974 are of too low accuracy to be of much use. All Oxford work in lead isotope analysis applied to archaeology postdates 1976 and has the requisite modern precision and is moreover on an absolute basis by reference to the NBS lead isotope standards. This applies also to work on lead isotopes applied to archaeology made by Schmitt-Strecker and Begemann at the Max-Planck-Institute for Chemistry at Mainz and by Emil Joel of the Conservation Analytical Laboratory (Smithsonian Institution), who makes her analyses at NIST using the methods of Barnes et al. (1973).

3.4. Chemical extraction of lead for mass spectrometry.

Thermal ionization mass spectrometry is sensitively dependent on the chemical purity of the lead loaded onto the filament. The presence of other elements can greatly reduce both the accuracy and the sensitivity of the measurements, so that careful and time consuming chemical separation of lead from the ore or artifact is necessary prior to isotopic analysis. Figure 5 shows a schematic flow diagram of chemical extraction of lead from the usual types of materials encountered in archaeological research. If a computer controlled mass spectrometer fitted with a 16 sample turret is used, sample purification is the step which limits throughput. If ores or artefacts with trace lead contents are to be analysed, then the blank level has to be controlled (to below 1 ng) by the special preparation and use of ultrapure reagents (Mattinson 1972) and by conducting the chemical separation in an over-pressured ultraclean (Class 100) laboratory. Such low blank levels can be achieved by lead separation methods based either on electrodeposition (Arden and Gale 1974) or by using anion ion exchange columns (e.g. Göpel et al. 1985), or a combination of both.

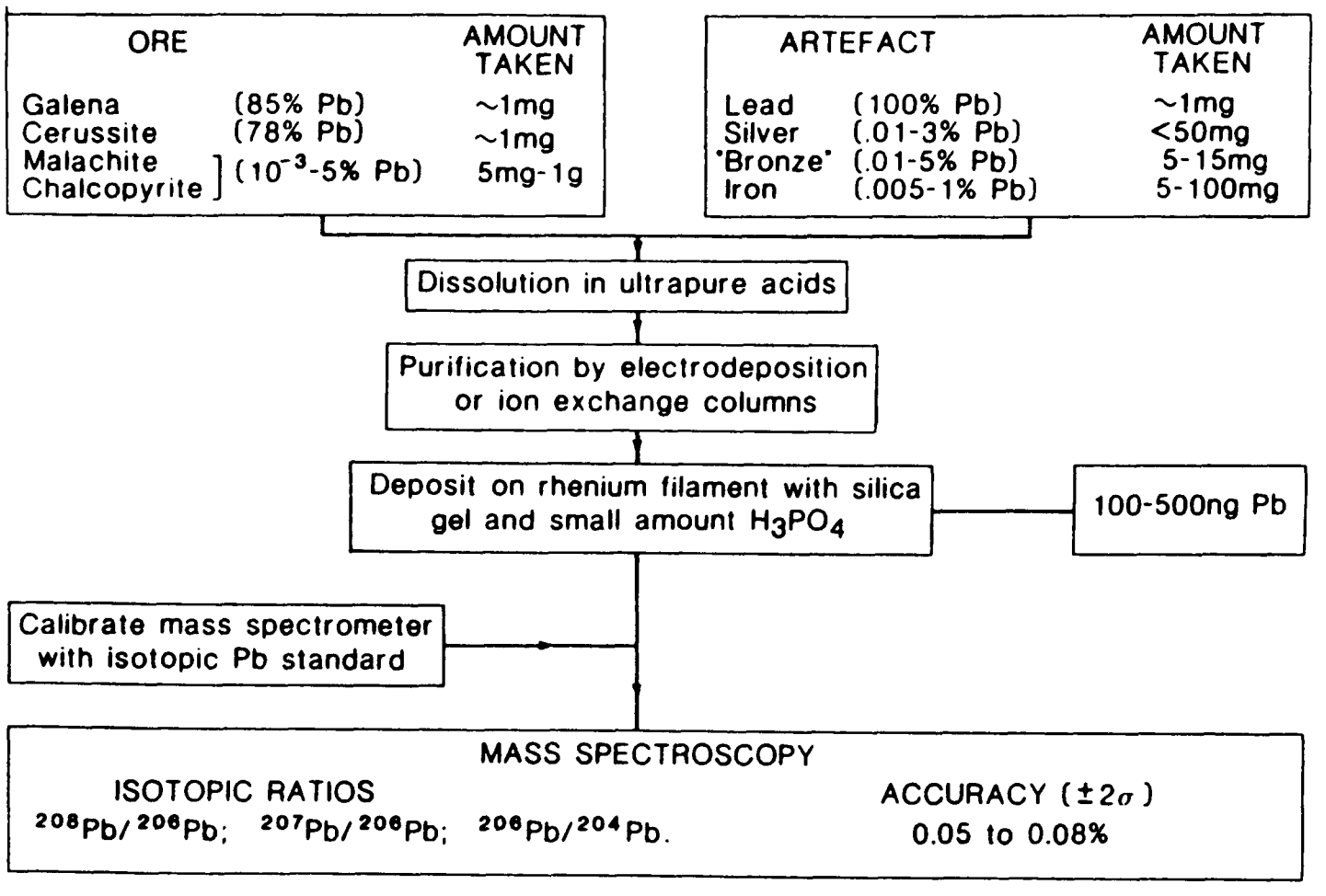


Fig. 5. A flow-chart of the chemical separation of lead from specimens used in archaeological work.

3.5. Interlaboratory comparisons.

Nowadays it is possible for any well equipped laboratory, using the silica gel technique, to measure routinely lead isotope ratios with absolute 2σ errors of 0.05 to 0.08% on samples of the order of 100 nanograms of lead. As examples of what can now be achieved in any good laboratory one can mention data for an absolute lead isotope standard published by the Oxford laboratory (Chamberlain and Gale 1980) and the laboratory in Mainz (Pernicka et al. 1984, Figure 24). This shows not only that the isotope ratios can be measured to better than $\pm 0.1\%$, but also that measurements can be corrected for fractionation to absolute values by reference to the lead isotope standard. This is very important

since it allows lead isotope measurements from different laboratories to be used together. An example of the comparison of lead isotope ratios for the same samples measured in different laboratories has been published previously (Gale 1989, p. 474, Fig. 3). It compares data obtained in Mainz and Oxford for archaeological objects from Troy; both sets of samples were taken on different occasions from the SAM collection of metal samples at Stuttgart. The difference in measurements could be estimated theoretically to be occasionally as much as 2 parts per mil, since each laboratory can measure to ± 1 part per mil. In fact the agreement is excellent for all three isotope ratios, with most measurements agreeing to within ± 1 part per mil. For our laboratory in Oxford a number of comparisons have also been made with the U.S. Geological Survey Laboratory in Denver, with agreement always better than ± 1 part per mil.

3.6. New developments.

Considerable effort has been spent in attempting to use other types of ion sources for which chemical separation techniques are minimized; special mention must be made of the use of an inductively coupled plasma (I.C.P.) used as the ion source for a quadrupole mass spectrometer (Date and Gray 1983 a and b). At present the sensitivity attained is comparable to that for the silica gel thermal ionization magnetic sector mass spectrometer, but the new technique appears to have much poorer accuracy (of the order of 1%) due to substantially larger and less reproducible mass fractionation, and to inaccuracies due to triangular peak shapes. Most archaeological problems, in common with those of isotope geochemistry, need the best achievable accuracy so that at the present stage of development the new techniques, though excellent for trace chemical analysis, are not suitable for lead isotope analysis. However an instrument is now being developed by the British firm VG Isotech which couples an I.C.P. source with an electric sector/magnetic sector mass spectrometer equipped with multicollection (see the next paragraph); using a mass discrimination correction method based

on the addition of Thallium to the sample and simultaneous measurement of the $^{205}Tl/^{203}Tl$ ratio (Ketterer et al. 1991) the accuracy of lead isotope measurement is already approaching that attained using thermal ionization mass spectrometry. The expected great cost of these new instruments is, however, likely to restrict their application to archaeology.

A considerable advance has been made in the direction of allowing accurate isotopic composition measurements on samples of as little as 1 to 10 nanograms of lead by developing multicollector thermal ionization mass spectrometers. McKinney et al. (1950) used a double collector mass spectrometer more than thirty-five years ago and achieved a precision of 0.01% by measuring the ion beams from two isotopes simultaneously using twin collectors. This technique compensates for fluctuations of thermal emission, eliminates problems due to the decay of emission and, by eliminating peak jumping, utilizes all the ions emitted. It is a technique which raises the sample throughput rate and enhances the internal reproducibility of isotope ratio data for small samples. There are now excellent commercial automated mass spectrometers which are fitted with up to seven adjustable and two fixed Faraday cups plus a Daly detector or a secondary emission electron multiplier to detect very small ion beams. Roddick and Loveridge (1986), using such a system for measuring radiogenic lead from zircon samples, demonstrated precision and accuracy of better than 0.1% for samples of lead down to about 0.5 nanograms.

A more accurate technique has been successfully used recently, with the latest multicollector mass spectrometers, of a $^{202}Pb - ^{205}Pb$ internal tracer against which to correct fractionation in the mass spectrometer. For all lead isotope ratios this reduces the absolute 2σ error between successive measurements to $\pm 0.01\%$, an order of magnitude reduction in absolute uncertainty. (Todt et al. 1984). The tracer is very expensive and in short supply; it has not yet been used in archaeological applications.

3.7. Double focusing mass spectrometers and the Oxford VG 38-54-30.

In 1987 Edwards, Chen and Wasserburg of the California Institute of Technology published a seminal paper on the application of mass spectrometric measurements of isotopes of U and Th for dating of corals by the U-Th disequilibrium method. The authors of the paper concluded that by applying mass spectrometry instead of alpha counting to measure the amounts of U and Th isotopes, the accuracy of measurement can be increased by two orders of magnitude and sample size reduced by the same factor. The main problem, however, for datable materials other than corals, lies in the measurement of the $^{230}Th/^{232}Th$, where the ^{230}Th beam is usually only a few ppm of the ^{232}Th beam. This publication stimulated great interest of geologists in mass spectrometers which could measure extremely high (in the range of 10^5) ratios of isotopes in very small samples. Patrick Turner, the chief scientist and designer of Vacuum Generators, one of the two leading firms manufacturing mass spectrometers, suggested that the way to increase the abundance sensitivity of their machines was by using a two or even three stage focussing system. The abundance sensitivity is defined in the VG literature as the ratio of the height of the tail of the peak at unit mass separation from the peak, to the hight of the peak itself. In a thermal ionization mass spectrometer with a 30 cm radius magnet, the abundance sensitivity defined in this way will be typically a few ppm for masses over 200 (it is 10 ppm for the Wasserburg's instrument). It has been proved by VG that this abundance sensitivity can be improved by an order of magnitude by adding after the magnetic analyzer a 38 cm electrostatic analyzer, without reducing the transmission. The dispersion length of the beam in this geometry is only 325 mm and there is not enough space to transmit more than one beam at a time through the electrostatic sector; therefore in this system only single collector measurements are possible. For multicollection in the double focussing mode it

is necessary to use a reversed geometry: first electrostatic and then electromagnetic analyzer (forward geometry Nier-Johnson configuration). The dispersion length of the beam in this case is 540 mm. This geometry has been applied in the design of Oxford VG 38-54 Isolab mass spectrometer.

In such a double focussing mass spectrometer the beam of ions undergoes direction and velocity focussing. The electrostatic analyzer provides filtering of scattered particles and accepts a small dispersion of ion energies from the ion source. Turner estimated that to obtain in this configuration abundance sensitivity below 1 ppm it is necessary to maintain a pressure of about 10^{-10} mbar in the final magnetic stage, but emphasized the role of the electrostatic analyzer as a 'differential pumping stage' between the source and the magnetic analyzer, which should help in achieving this goal, because of the importance of pressure on the ion-molecule scattering of ions.

Velocity and direction focussing.

If a very narrow beam of ions of identical specific charge e/m, but heterogeneous energy, enters a radial electrostatic field with negligible angular divergence (emerging from a slit) it undergoes *velocity dispersion.* Therefore, ions of different velocities follow different paths after emerging from the field. They are brought to a *direction focus* at the intermediate point at the same distance from the exit boundary of the field, but laterally displaced from one another.

A radial electric field deflects ions according to their kinetic energy:

$$F = eE = \frac{mv^2}{r} \tag{3.9}$$

therefore $r = \frac{mv^2}{eE}$ (3.10)

where E represents the radial electric field

After passing through an intermediate slit, this divergent beam is subsequently allowed to enter a homogeneous magnetic field in which ions of different

velocities again suffer deflections. Then ions of similar e/m (specific charge) but differing in energy recombine at a single point after emergence from the magnetic field. This is the point of *velocity focussing.* If the initial beam is comprised of singly charged ions of different masses, the ions undergo mass analysis by the magnetic field, and ions of different masses converge to different velocity focussing points after emerging from the magnetic field. The ions of different velocity groups that enter the magnetic field with a small angular divergences are brought to a direction focus at a point on the direction focusing curve. Ions of different specific charges are focussed at different points, both on the velocity focusing curve and the direction focusing curve.

The condition of double focussing requires that the velocity dispersion of the ions in the electrostatic field must be exactly compensated by the magnetic field. The velocity focussing curve and the direction focusing curve at the exit of the magnetic analyzer are different from one another, but the two curves might be made to intersect with an appropriate combination of the fields. Those ions which are focused at the point of intersection of those two curves are said to undergone double focusing by the combined electric and magnetic fields. The principle is not new and was, for instance, used by Nier in 1953 to build a high resolution mass spectrometer for precise atomic mass measurements (McDowell 1963, 238-242).

Figure 6 shows a schematic diagram of the Oxford double focussing VG 38-54-30 mass spectrometer. The source [1] of this machine houses a 16 sample turret and after the change of samples is pumped first by a rotary pump (opened by valve V_r) followed by a cryopump (opened through a gate valve V_g). A vacuum of the order of 10^{-8} mbar is achieved in the source chamber in about 40 minutes. During the turret change the source is filled with dry nitrogen to keep the water vapour in the source to a minimum (cylinder with nitrogen is connected through V_n). High voltage cables go through the side of the source

chamber and are connected to the series of source slits [S] which are positioned at the entrance of the flight tube on the left hand side of the chamber. The flight tube then curves through the 38 cm radius electrostatic analyzer [2], goes through the intermediate focus slits [3] and curves between the poles of the magnet [4] of 54 cm effective radius. The ions are collected in a multicollector system [5]. Multiple collectors form an adjustable array of seven motorized Faraday cups. The axial collector [7] has a fixed horizontal position, but can be withdrawn to allow ions to pass through a further 30 cm electrostatic lens to a Daly detector for single ion counting (Daly 1960). The ion currents from the Faraday cups are amplified [6] and recorded in a digital acquisition unit. The whole machine is fully computer-controlled. Multiple collection enables simultaneous measurements of several ion beams, removing errors caused by fluctuations of beam intensity in the peak jumping mode. Our experience at Oxford shows that measurements taken with the old 12" single collector mass spectrometer used for archaeological work until the end of 1988 had running errors rather higher than the new VG machine, and required much more time per analysis. The technical specification of the Oxford VG 38-54-30 double focussing mass spectrometer and the statistical evaluation of lead isotope data of NBS 981 lead standard run between January and April 1992 is in Appendix 1. Standard deviations of the mean from 69 runs are .00159 for $^{208}Pb/^{206}Pb$, .000402 for $^{207}Pb/^{206}Pb$ and .0083 for $^{206}Pb/^{204}Pb$. The *Wilk's* statistics (Shapiro and Wilk 1965) shows for all three ratios $W > 0.92$ which testifies normal distribution of the data.

The machine at Oxford is a modified version of the standard VG Isolab 54. The pumping system has been improved by the use of two rotary pumps for the roughing of the source and pumping of the amplifier housing, several large ion pumps placed along the flight tube and a large 3000 l/s Titanium Sublimation pump (TSP) and a Perkin Elmer Boostivac combined ion plus TSP plus

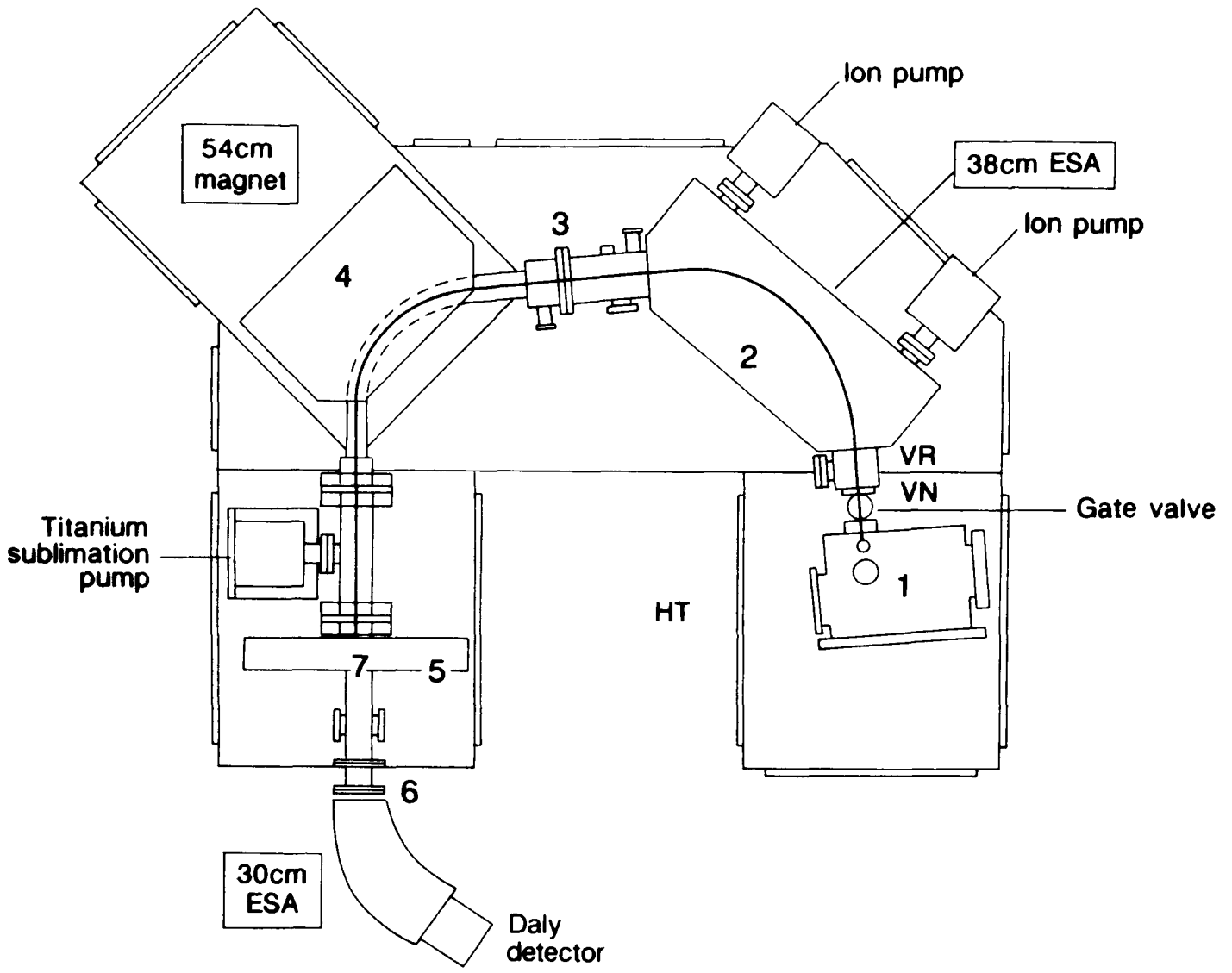


Fig. 6. Schematic diagram of the Oxford double focussing mass spectrometer: 1. Source, 2. Electrostatic Analyzer, 3. Intermediate Focus Slits, 4. Magnetic Analyzer, 5. Multicollector System, 6. Amplifier, 7. Axial Faraday collector.

cryoshield pumps working at the collector end. In January 1992 the instrument was substantially modified by the addition of a third focussing stage consisting of a 30cm electrostatic lense and a second axial collector. This configuration improved greatly the abundance sensitivity of the machine, which at present (measured at the pressure of 5×10^{-9} torr at the collector end) is 0.2 ppm for mass 237 relative to mass 238, at a resolving power of 400. This arrangement allows a measurement of two isotope peaks different by one mass unit, which differ in the intensity by the factor of 10^5, without the interference of the larger peak on the smaller peak.

Phot. 1. VG double focussing mass spectrometer in the Isotrace Laboratory, Oxford.

4. ISOTOPE MEASUREMENTS IN GEOCHRONOLOGY.

4.1. Historical introduction.

The radioactivity of uranium and thorium was discovered in the last decade of the 19th century by Becquerel (1896) and Maria Sklodowska Curie and her husband (Curie and Curie 1898). Subsequent work on the radioactive decay series of uranium and thorium showed that there are several kinds of radiothorium which decay at different rates. Richards and Lambert (1914) found that lead produced by the decay of uranium had a different atomic weight than ordinary lead; they had already shown that the atomic weights of natural elements are not whole numbers. These and similar problems led Frederick Soddy (1911, 1914) to suggest that chemical elements are in general composed of isotopes, that is, atoms having the same chemical properties but differing mass. J.J. Thomson directly proved that this was so for neon in 1913. Aston, also working in the Cavendish Laboratory, immediately set out to build ever more sophisticated mass spectrographs to extend this finding to other elements, but it was not until 1927 that he directly proved the existence of the isotopes of lead (Aston 1942).

In 1905, even before the discovery of isotopes, Rutherford and Boltwood had independently recognised that radioactivity could provide a method of measuring the ages of rocks and minerals. By 1907 Boltwood had made the first crude estimates of the ages of three uraninite samples based on their U/Pb ratios. By 1929 Rutherford was able, on the basis of the uranium-lead decay scheme, to estimate the age of the earth and to get it right within a factor of two. In the late 1930's Nier perfected the first mass spectrometers capable of relatively high precision and ushered in modern lead isotope studies. Subsequent to 1945 geologists and geochemists have been ever more active in using the uranium-lead and thorium-lead radioactive decay schemes. They have used them not only for measuring geological time but they have also used lead isotope compositional

variations as a tracer and provenance indicator for ores and minerals in studies of ore genesis and petrogenesis.

Consequently it was discovered that small variations which exist in the isotopic compositions of many of the common elements are significant in explaining the geological, biological and chemical histories of rocks, minerals and organic materials. The major cause of variations in the isotopic composition of radiogenic elements is the natural radioactive decay of parent isotopes. The rate of decay can be measured and used to calculate the time since the beginning of the process. The reason for natural variations in the relative proportions of non-radiogenic isotopes lies in their fractionation by physical, chemical and biological factors. The isotope variations reflect the geological histories of the rocks and minerals in which they are found and they can give quantitative information about processes and conditions in different geological environments. The research in this field, initiated by Aston and Nier in the thirties, developed in the sixties into a new branch of geology - isotope geology.

Isotopes of many elements are used today in geology for dating and tracing the history and mode of formation of rocks and minerals. Isotope geochemistry and geochronology brought about a revolution in the study of Earth Sciences. Studies of variations in the isotope compositions of Pb, Sr, Nd, Hf, Ar and other elements, allowed the construction of an absolute chronology (not hitherto available) stretching back for 4, 500 million years. In another direction the isotope geochemistry of these and other elements proved to be significant in the study of fundamental questions of petrogenesis, the origin of the elements and the origin and the evolution of the solar system.

The same isotope variations can be used for different purposes in archaeological research. For example the isotopic composition of C, N, Sr and Pb in animal and human bones will reflect, through food intake, the environment in which they lived. Raw materials like marble, gypsum and metals commonly

used in antiquity also carry unique isotopic "fingerprints" characteristic of the geological deposits from which they came.

4.2. Isotope geochemistry of common lead in ore deposits.

Lead is an ubiquitous constituent of ore deposits, rocks and minerals. Lead is present in major amounts in lead-zinc and lead-silver ore deposits and in lesser amounts in copper and iron ore deposits; it occurs in at least parts per million levels in all rocks and non-metallic minerals. This would be of no significance for geochemistry or for archaeology but for the fact that the isotopic composition of naturally occurring lead is variable.

Variations in the lead isotope composition of minerals of different origin were measured for the first time nearly eighty years ago. As early as 1914 Soddy and Hyman showed that lead from a Ceylon Thorite had an atomic weight approximately one unit greater than common lead. This result verified earlier predictions that lead 208 is formed as a daughter product of the decay of ^{232}Th, whilst ^{206}Pb and ^{207}Pb are stable end decay products of ^{238}U and ^{235}U respectively (see Chapter 2 for a fuller explanation). It is known now that all lead metal present in the earth's crust in all terrestrial minerals consists of four isotopes. Three of those isotopes are radiogenic daughters of uranium and thorium (^{208}Pb, ^{207}Pb and ^{206}Pb) and one is the primeval stable lead isotope (^{204}Pb).

$$^{238}U \longrightarrow \frac{8\alpha}{6\beta} \longrightarrow^{206} Pb \qquad (T_{\frac{1}{2}} = 4468my)$$

$$^{235}U \longrightarrow \frac{7\alpha}{4\beta} \longrightarrow^{207} Pb \qquad (T_{\frac{1}{2}} = 704my)$$

$$^{232}Th \longrightarrow \frac{6\alpha}{4\beta} \longrightarrow^{208} Pb \qquad (T_{\frac{1}{2}} = 14010my)$$

In 1947 Nier reported isotopic analyses of lead extracted from galenas from different ore deposits which demonstrated conclusively that such leads have variable isotopic compositions. On the basis of these results Nier concluded that those variations result from mixing of the radiogenic lead with primordial lead prior to the deposition of the galenas. Therefore the isotopes 208, 207 and 206 are composed of a mixture of their primaeval concentrations and the radiogenic additional concentration. That means that the number of atoms of lead 206 added between time t_0 and the present is:

$$D_{206} = N\left(^{238}U\right)\left(e^{\lambda_{238}t_0} - 1\right) \tag{4.1}$$

In a similar way the amount of lead 207 and 208 will increase through the decay of ^{235}U and ^{232}Th for as long as those isotopes are present in the mineral containing the lead, or its formative fluids.

The early uranium and thorium ages were estimated from chemical analyses of the total amounts of lead, uranium and thorium in highly radioactive minerals. Later the development of mass spectrometers made it possible to separate and measure the amount of individual lead isotopes. The terrestrial isotope ratio of $^{238}U/^{235}U$ has been measured and it is known to be constant at 137.88 (Gulson 1986, p. 14). Therefore from (4.1):

$$\frac{N_{206}}{N_{207}} = \frac{137.88(e^{\lambda_{238}t} - 1)}{e^{\lambda_{235}t} - 1} \tag{4.2}$$

From the above equation and the Holmes-Houtermans model applied to lead minerals, one can calculate the value of t_0 to be about 5×10^9 and in this way lead isotope ratios were the first means of estimating the earth's age (Nier 1939, Holmes 1946). Previous geological attempts at establishing a time-scale for the evolution of the Earth were based on such approaches as making estimates of the rates of sedimentation of clays and of the amount of salt brought down to the oceans by rivers. In 1942 Gerling published the first calculations of the age

of the earth based on the variations of the abundances of lead in lead minerals. In 1956 Patterson evaluated the assumption that the age of the Earth is similar to that of meteorites. Further research into this method of dating, particularly in the last two decades by combining the terrestrial and meteoritic lead isotope measurements, established that the earth was created 4.57 thousand million years ago (Tatsumoto 1975).

A simple method of dating of ore deposits using the measurements of lead isotope ratios is the 'common-lead' method of dating (Faure 1986, p.309-320). 'Common' lead occurs in minerals which have U and Th concentrations much lower than their lead concentration. Practically all galenas and other sulphides of base metals contain common lead. Their U/Pb and Th/Pb ratios are so low that their lead isotopic composition does not change appreciably with time, providing that they remain in a closed system, where there is no more U and Th entering the mineral. The common lead dating method is based on the evolution of lead since the time when the earth started to act as a closed system for U, Th and Pb, to the time when the lead was isolated from its radioactive parents during mineral formation. Due to their chemistry U and Th largely separate from Pb during geochemical processes, such as the formation of ore deposits.

The earliest general model for evolution of common lead was introduced by Holmes (1946) and Houtermans (1946); it is known as a single stage growth model and was based on several assumptions:

1. Originally the earth was fluid and homogeneous.
2. At that time U, Th and Pb were uniformly distributed.
3. The isotopic composition of primeaval lead was everywhere the same.
4. Subsequently the earth became rigid and small regional differences arose in U/Pb and Th/Pb ratios.
5. In any given region the U/Pb ratio changed only as a result of radioactive decay of U to Pb.

6. At the time of formation of a common lead mineral the lead was separated from U and Th and its isotopic composition has remained constant since that time.

However, the radioactive decay of U and Th before the ore formation and later geological processes have greatly changed and diversified the isotope composition of the Earth's lead from its original (primordial) values, but assuming a common origin of the solar system and its meteorites, one might expect to find primordial lead in the U and Th free phases of meteorites. In 1953 Patterson indeed first measured in the troilite phase of the Canyon Diablo meteorite (troilite is an iron sulphide with extremely low U and Th concentrations) the lowest observed lead isotopic ratios:

$$^{206}Pb/^{204}Pb = 9.307 \tag{4.3}$$

$$^{207}Pb/^{204}Pb = 10.294 \tag{4.4}$$

$$^{208}Pb/^{204}Pb = 29.479 \tag{4.5}$$

These lead isotope compositions are accepted as the primordial isotope ratios of lead at the time of the creation of the Earth (Tatsumoto et al. 1975).

The simplest possible history for, say, a galena is that the parent material for the galena suffered no chemical fractionation of U and Th from Pb from the time t_p for formation of the Earth until production of the galena t: such a history is referred to as single-stage growth of lead in a closed chemical system. It can be characterized by single-stage growth curves with associated μ value $^{238}U/^{204}Pb$ as measured today for the parent U-Pb system: and W value $^{232}Th/^{204}Pb$ for the parent Th-Pb system (Köppel and Grunenfelder 1979). The growth curves originate at time t_p from an initial primaeval lead isotope composition defined in

practice by that of the lead in the troilite phase of the Canyon Diablo meteorite. This model is the previously mentioned Holmes-Houtermans model (Holmes 1947, 1949). From this model it is possible to compute, from the measured lead isotope compositions of ore deposits, so-called model ages which should give the geological age of the ore deposit if the model assumptions are satisfied (Köppel and Grunenfelder 1979). In this model the growth of the lead isotope ratios is described by the following equations which give the isotope ratios of a sample of Pb withdrawn from all U and Th at geological time t measured from t_p, the time of formation of the Earth:

$$\left(\frac{^{206}Pb}{^{204}Pb}\right)_t = \left(\frac{^{206}Pb}{^{204}Pb}\right)_{t_p} + \mu\left(e^{\lambda_8 t_p} - e^{\lambda_8 t}\right) \tag{4.6}$$

$$\left(\frac{^{207}Pb}{^{204}Pb}\right)_t = \left(\frac{^{207}Pb}{^{204}Pb}\right)_{t_p} + \frac{\mu}{137.88}\left(e^{\lambda_5 t_p} - e^{\lambda_5 t}\right) \tag{4.7}$$

$$\left(\frac{^{208}Pb}{^{204}Pb}\right)_t = \left(\frac{^{208}Pb}{^{204}Pb}\right)_{t_p} + W\left(e^{\lambda_2 t_p} - e^{\lambda_2 t}\right) \tag{4.8}$$

where $\left(^{206}Pb/^{204}Pb\right)_{t_p}$ etc. are the primordial lead isotope ratios and λ_8, λ_5 and λ_2 are respectively the radioactive decay constants for ^{238}U, ^{235}U and ^{232}Th.

These are closed-system evolution equations currently used in the lead isotope age and model calculations. The lead isotope composition for the galena at the present day is obtained by setting $t = 0$. The method of dating of geological formations based on the principles outlined above is called the 'Common lead dating method'. Figure 7 presents a single-stage growth curve of selected stratiform sulphide deposits. T denotes the time when the original solar system gaseous nebula, with uniform U/Pb and Th/Pb ratios and an isotopically homogeneous lead, differentiated into the present solar system bodies with distinctly different U/Pb and Th/Pb ratios.

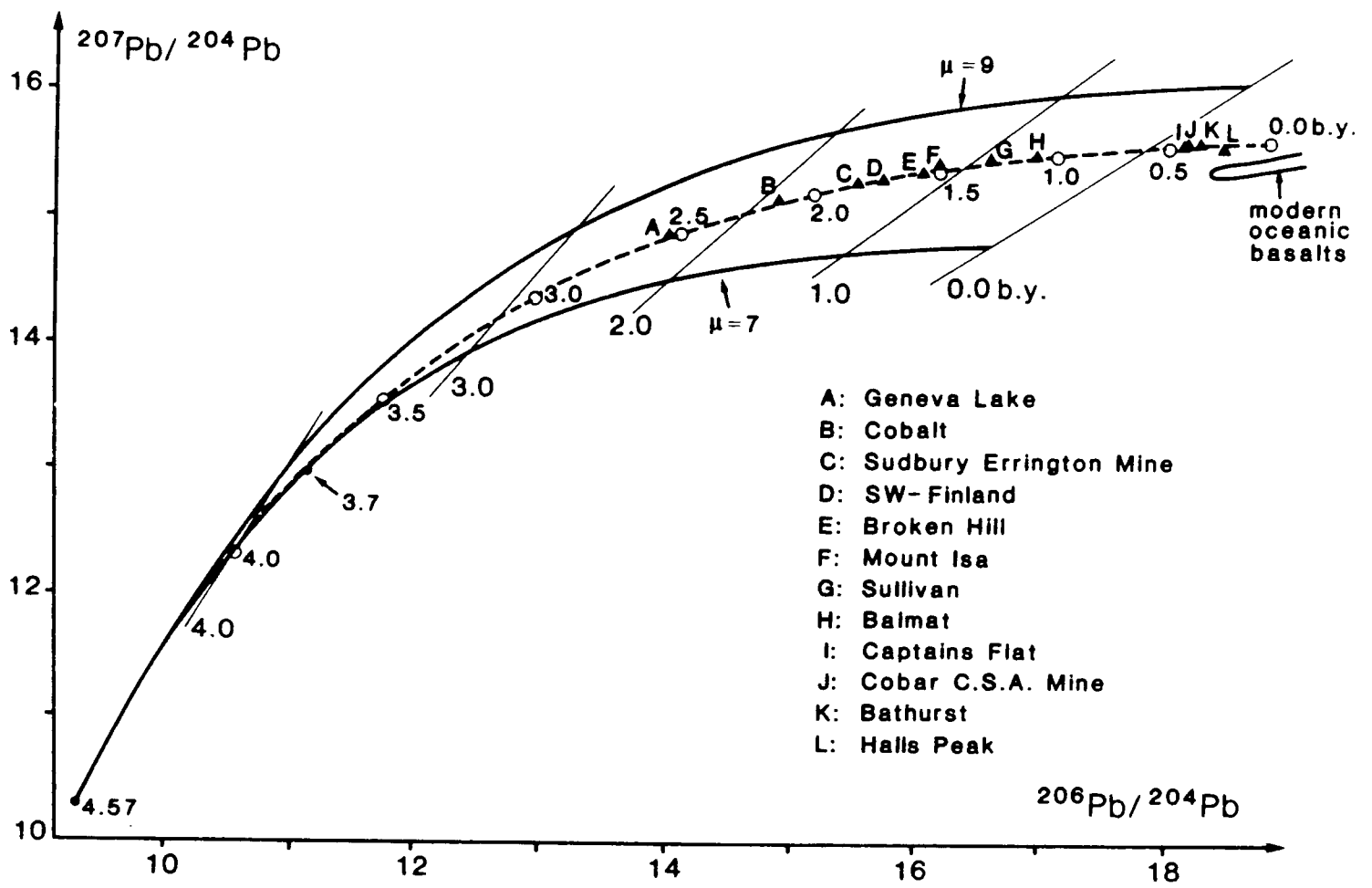


Fig. 7. A single-stage growth curve of some stratiform ore deposits. The curve starts at 4.57 billion years (the age of the Earth) and the isotopic composition of lead at time $T = 4.57$ is the primordial composition. The lead isotope ratios of younger deposits depend on the amount of U and Th in the ore forming fluids, which is measured by μ for the U-Pb system. The straight lines are isochrones for selected values of t.

In practice the lead of most ore deposits will have a complicated history involving, for example mantle residence, a period of crustal residence accompanied possibly by metamorphism, erosion and sedimentation, until the lead was finally extracted during a volcanic cycle or by the action of hot brines and concentrated in an ore deposit. Later models of the terrestrial evolution of lead isotopic compositions (Doe and Zartman 1979; Amov 1983) have attempted to take account of these complications.

4.3. Lead isotope evolution of ore bodies and the principles of U-Th-Pb dating methods.

The decay of U and Th to stable isotopes of Pb is the basis for several important methods of geological dating. The most commonly used at present are the isotopic U, Th-Pb concordia methods and the uranium-lead method.

In all dating methods based on measurements of the parent-daughter systems it is essential that the chemical system which includes measured isotopes can be regarded as closed to any outside influence. Lead isotope measurements are also used in mineral exploration (Gulson 1986). The principles of this application are based on two observations: that the lead isotope pattern of mineralization differs from the barren country rock and that the isotopic composition of lead is not changed by the isotopic fractionation during natural physical and biological processes such as weathering.

In the ideal case for dating, a crystallizing material should incorporate only the element with the radioactive isotope, the mother element and no daughter isotope; in that case the amount of daughter isotope measured at a particular time after crystallization must have come purely from radioactive decay of the mother isotope. Another assumption essential for dating is that immediately after mineral formation the content of these two elements has been changed only by radioactive decay. The first assumption is hardly ever realised, and the second is only rarely realised.

Ore deposits can be classified into two broad groups: syngenetic ores, which were deposited at the same time as the rocks surrounding them, and epigenetic ores which were deposited later than the time at which the rocks in which they are found were formed. Syngenetic ores are stratiform, that is they follow the general stratification of their host rocks. Epigenetic ores can be stratiform too, but more usually they follow fractures, joints, faults and other weaknesses and cut across sedimentary or other primary layering. Some ores occur only

within a specific stratum in an orefield; they are stratabound. Geochronologists have discovered that only the stratiform deposits (sandwiched between sedimentary rocks) fall on or near the single stage dating curve or the modern variants of that developed by Stacey and Kramers (1975) and Cumming and Richards (1975). From the equations expressing the temporal growth of radiogenic lead isotope compositions it is possible to calculate model ages for given ore deposits (Russell and Farquhar 1960, Gulson and Mizon 1979, Cumming and Richards 1975). The Cumming- Richards model agrees quite well with other geochronological methods for dating strata-bound (conformable) sulphide deposits (other isotope methods of dating: Rb-Sr, Sm-Nd; see Faure 1988), but the Amov (1983) model provides even better model ages.

Geological literature gives examples of many ore deposits, especially the so-called strata-bound (Faure 1977, pages 235-237, 253) or conformable ore deposits, which seem to have lead isotope compositions which vary very little indeed throughout the whole deposit. In some cases the variation is as little as 0.1%; an example is the Bleiberg deposit in Austria (Köppel and Kostelka 1976). Quite often the variation in lead isotope composition of ores in one mine is less than 0.3%; an example from the Amelia mine in the Upper Mississippi Valley ore district is given in Figure 8 (Heyl et al. 1966). Such ore deposits commonly have lead isotope compositions which lie close to a single-stage model (Faure 1977, p. 227) evolution curve as was first noticed by Stanton and Russell (1959, pages 288-607). Many of these, possibly syngenetic, lead ore deposits are apparently associated in a conformable way with rocks of island-arc-volcanic affiliation. Since near-surface concentrations of U, Th and Pb are very heterogeneous, the conformable ores were suggested to be the product of a lower-crustal or upper mantle environment. The single-stage growth curve passing through these lead ore deposits, each of which exhibits a very uniform lead isotopic composition, has come to be known as the primary growth curve for terrestrial lead.

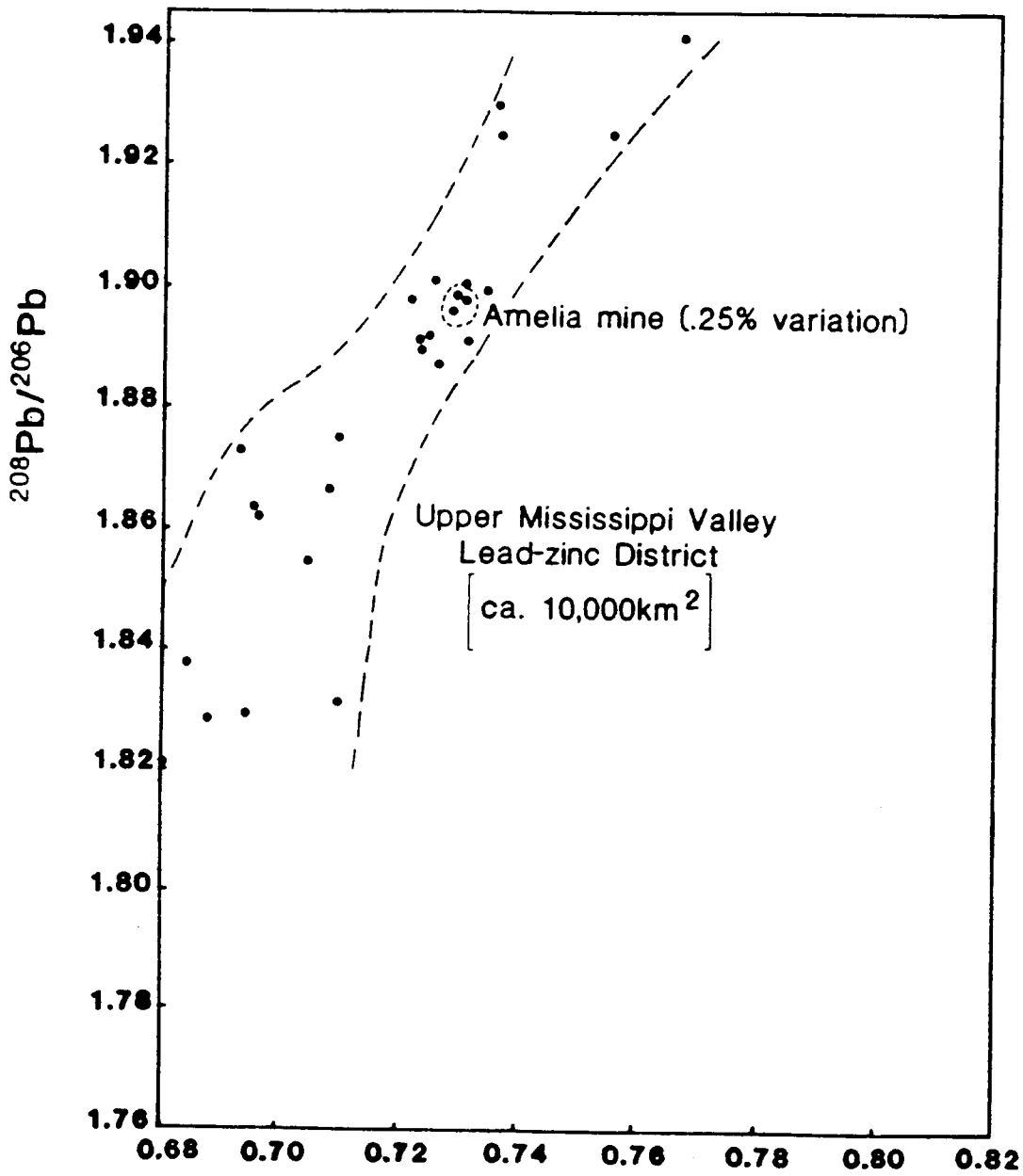


Fig.8. Lead isotope composition of galenas in Upper Mississippi Valley and from the Amelia mine.

Figure 9 shows how certain deposits due to alterations after the initial time of ore formation can be dramatically removed from the dating curve. The section of the Cumming and Richards dating curve on this figure covers the age range of the last 2.5 billion years; the deposit of Ivigtut, for example, dated by other methods to 1.1 Ba shows lead isotope ratios quite outside the curve and nearest to about 2.5 Ba. However, such deposits are very rare. A more common situation is represented on this graph by the deposits of Rosebery and Rammelsberg, which plot only a little off the Cumming-Richards curve. For this reason it is generally possible to predict the geological age of a deposit from its lead isotope composition.

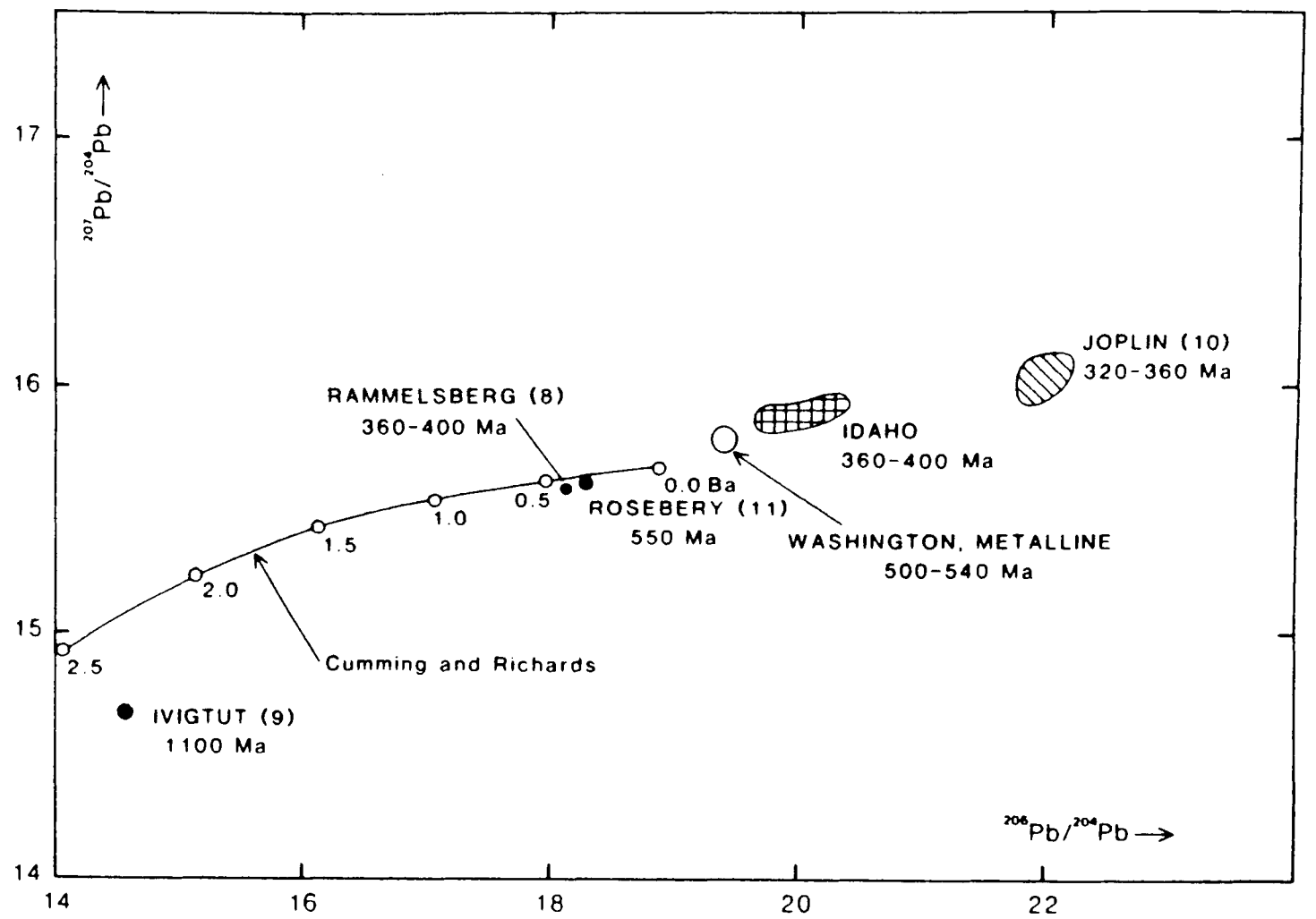


Fig. 9. The common lead dating curve based on the Cumming-Richards model of dating and lead isotope compositions of ore deposits altered after the initial time of ore formation. The deposits of Ivigtut, Joplin, Metalline and Idaho display lead isotope compositions altogether outside the single-stage growth curve.

Figure 10 shows on an expanded scale the lead isotopic compositions, in relation to the Cumming-Richards growth curve, for some individual groups of deposits which are typical of the many ore deposits which have now been investigated by the geologists. Some of these deposits have isotopic compositions well away from the growth curve for conformable leads; some deposits, such as the Indonesian island ore deposits, have isotopic 'fields' which cross the growth curve. Yet other deposits have isotopic compositions which plot to the right of the zero time point on the main evolutionary growth curve. As in Figure 9 here also some ore deposits have even more extreme lead isotope compositions which lie well beyond the zero time point of the Cumming-Richards growth curve.

Today it is accepted that the concept of a single-stage lead isotope his-

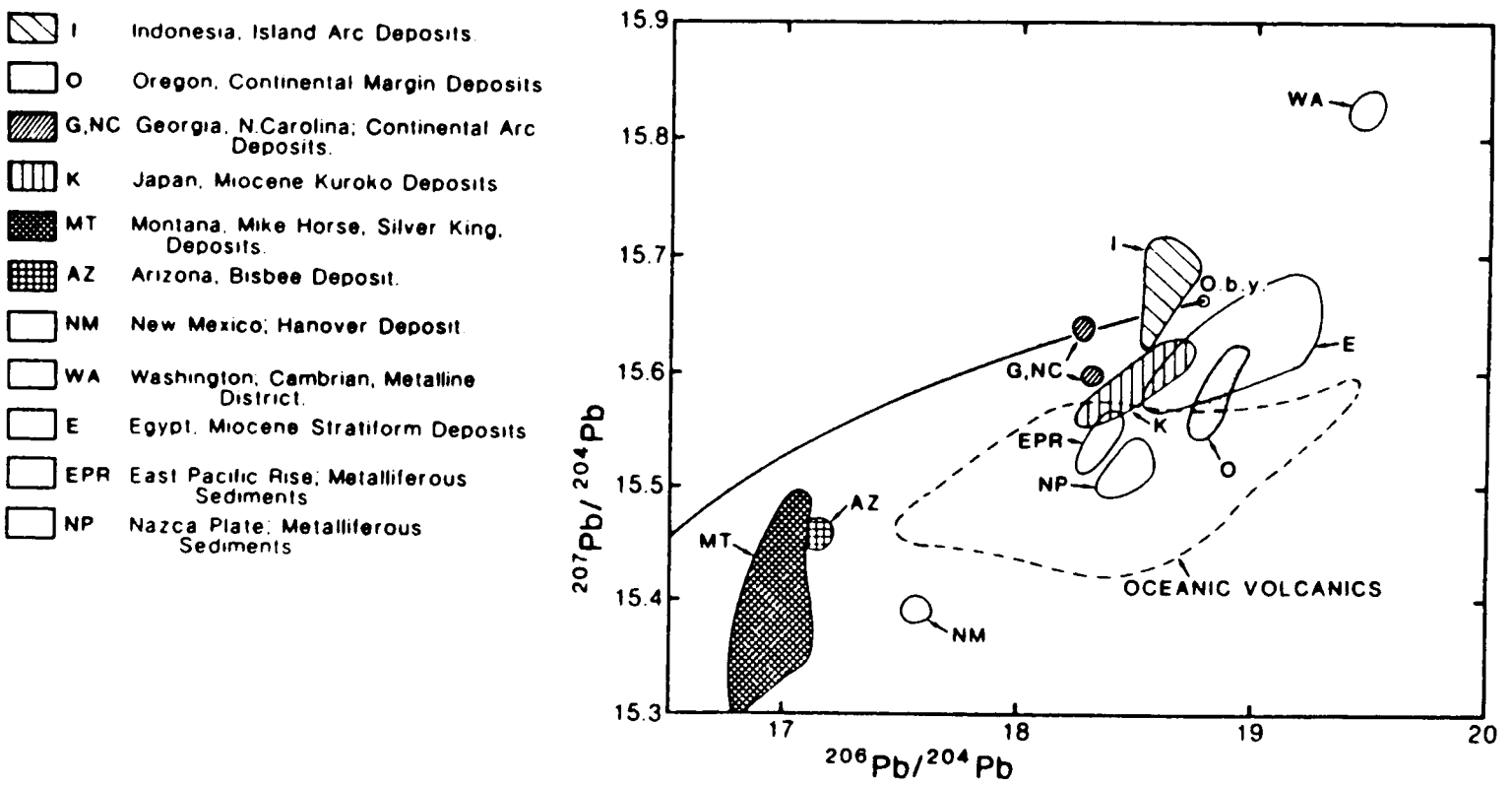


Fig. 10. A group of young ore deposits plotting outside the lead isotope dating curve.

tory cannot be correct for any real ore deposit; moreover analyses of volcanic rocks from oceanic regions showed that the mantle cannot be regarded as a uniform reservoir for U, Th and Pb. With the development of plate tectonics there came also a number of more complex lead isotope evolution models, involving differentiation and mixing processes. Improvements in the accuracy of measurement of lead isotope compositions brought about the redetermination of the primaeval lead isotope composition as recorded in the Canyon Diablo meteorite (Tatsumoto et al. 1975). This new primaeval lead isotope composition shifted the Holmes-Houtermans growth curve in such a way that it was no longer possible to fit the ore lead of strata-bound (conformable) deposits on a single-stage evolution curve such that their model ages agreed with the stratigraphic ages, especially for Phanerozoic deposits.

4.4. Recent models for lead isotope evolution.

Four new models have been proposed to accommodate the conformable ore deposits on revised growth curves. Stacey and Kramers (1975) introduced a two-stage model which involved a major first differentiation of the Earth into a crust and mantle at about 3.7 x 10^9 years ago, whereby the crust was enriched in U and Th with respect to the mantle. The effects of later differentiation within the crust or mantle were assumed to be largely obliterated by mixing processes. However, the nature of the fundamental event required by the model is not clear, though it may represent an approximation for a prolonged period of crustal formation which ended approximately 2.5 x 10^9 years ago. Cumming and Richards (1975) proposed another model which takes in the account the U/Pb and Th/Pb ratios: $\mu = {}^{238}U/{}^{204}Pb$ and $W = {}^{232}Th/{}^{204}Pb$ (present-day values). In this model μ and W increase linearly with time; they forced the growth curves through the data points of Canyon Diablo lead and of the Captains Flat (Australia) Pb-Zn-Cu deposit of Silurian age (430 Ma). The continuous linear increase of the μ and W values can be related to continuous differentiation processes, but the implied continuous linear increase of U and Th concentrations in the crust cannot, of course, occur forever in the real, as opposed to model, world.

Doe and Zartman (1979) suggested a rather elaborate multistage model of discontinuous evolution. Their "Plumbotectonics" model attempts to involve lead isotope evolution in different zones of the crust and mantle in connection with their dynamic development and interaction.

More recently Amov (1983) has constructed what is currently perhaps the most realistic model of conformable ore lead evolution, using a dynamic model of the continuous isotopic evolution of uranogenic and thorogenic lead. His model depends essentially on the assumption that the rate of change of μ and W (present-day values) increased initially and, after attaining a maximum,

decreased due to surface cooling of the Earth.

An important parameter in Amov's model is the time t_m, when the rates of change of μ and W attained their maxima; it depends on the age of formation of the different layers of the crust or, in mixing processes, on the participation of materials from the older or younger crust and mantle. The value of t_m (or a related parameter T) indicates the time of enrichment in U/Pb, which is an extremely important index for identifying the lead source-type.

Both of the 1975 models yield model ages for strata-bound sulphide deposits which agree quite well with geological ages and the ages obtained by other geochronological methods. Amov's model yields model ages which are in even better agreement with independently derived ages of such deposits, especially for the younger deposits.

All of these model ages calculations can be quite important for lead isotope provenance studies in archaeology and history of art, because from the measured lead isotope composition of an artefact a model age can be computed which will give a guide to the rough geological age of the ore deposit which supplied its metal (or pigment). The geological publications frequently include information about the geological ages of various deposits, so knowing the approximate age of the mineral which was used in making the ancient artefact one can estimate the possibility of the mineral coming from a given geographical area. This can be useful as a guide to which ore deposits should be investigated and included in further provenance studies. However, it must be emphasized that the lead isotope composition is related to the age of the ore formation only to a certain degree, because it is known that the lead isotope compositions of ore deposits of the same age can be different to a degree quite significant for provenance studies.

4.5. Variations in the lead isotope ratios in different deposits.

The variations in isotope composition characteristic of geographically and mineralogically different deposits arise from a number of processes. If it can be assumed that the initial terrestrial lead was contained in a large reservoir containing also uranium and thorium, a continuous production of radiogenic lead isotopes would be taking place in such a reservoir since the earth was formed 4570 Ma ago. If at some point in time lead was tapped from this reservoir to form a major deposit, leaving behind U and Th (which is the normal course of events during ore formation), and then the deposit remained undisturbed, its isotopic signature will remain frozen until the present day. If some thousand years later another large deposit is formed, then its signature will be different, because much more of ^{208}Pb, ^{207}Pb and ^{206}Pb was formed from U and Th during those thousand years. The mathematical formulae describing this process for the isotope ^{206}Pb can be presented as (Gulson 1986, p. 16):

$$present\ day\ lead = initial\ or\ common\ lead + radiogenic\ lead$$

or in a closed system with a fixed U/Pb ratio:

$$\left(\frac{^{206}Pb}{^{204}Pb}\right)_t = \left(\frac{^{206}Pb}{^{204}Pb}\right)_{ti} + \left(\frac{^{238}U}{^{204}Pb}\right)_n \times \left(e^{\lambda_8 t_i} - e^{\lambda_8 t}\right) \qquad (4.9)$$

where:

t_i is the geological time at which evolution of ^{206}Pb started,

t is the time elapsed since t_i and is the geological time since the evolution of ^{206}Pb ceased,

n is the present day U/Pb ratio,

λ_8 is the ^{238}U decay constant

Lead-rich ore systems contain relatively much less uranium than lead-poor systems like country rock. Therefore the lead isotope composition of the country rock and lead from the mineralization can be substantially different, because the

component of radiogenic lead isotopes will be much higher in the rock than in the lead rich mineral. Thus galena contains so much lead compared with U that the isotope ratios are the same as at the time of crystallization. In contrast some pyrites may contain amounts of lead which are comparable with concentrations of U in this mineral. In such a case the present day measured lead isotope ratios of such a pyrite represent the initial ratios plus a component of radiogenic lead from radioactive decay. Gulson (1986, pages 17-23) has discussed in detail various cases of lead/uranium ratios in the context of lead isotope research in mineral exploration; here this discussion is largely omitted since it is not relevant to the archaeological use of lead isotope ratios.

The discussion so far has to some extent assumed that a given ore deposit has throughout a single lead isotope composition; only some examples of deposits having a very small range of lead isotope ratios were quoted earlier from the geological literature. In fact it seems that most ore deposits are characterized by a small range in lead isotope ratios. Some of the possible causes of this small isotopic variability within a given ore deposit are as follows:

1. selective extraction of metals from their source rocks prior to their transport and ultimate deposition;
2. Pb which developed in several stages in the crust was incompletely mixed prior to deposition;
3. metamorphic events subsequent to the time of emplacement of an ore body - mixing with lead from country rocks;
4. it is possible that over geological time U has migrated towards the upper crust faster than Th and both in preference to lead - the evolution of lead in the lower crust and upper mantle is slightly different from that in the outer continental crust. Some ore deposits contain mixtures in varying proportions from these reservoirs;
5. in relatively rare cases the copper ores, say, may still contain uranium

(the decay of which causes the lead isotope composition to go on evolving after ore formation); variations through the ore deposit of the U/Pb ratio will then cause differences in lead isotopic composition.

Various, unusual modes of ore formation might also cause alteration of the lead isotope composition. For example copper, iron and lead sulphides can be formed by syngenetic (or contemporary) precipitation of metal from sea water. The Bass-Becking Institute demonstrated experimentally that metals could be accumulated on the sea floor by sulphide-reducing bacteria living in the upper parts of sea floor muds; metal concentrations in sea water as low as 0.5 ppm were enough to support this process. Bacteria take metals into their body as sulphides by reducing natural sulphate in sea water.Their bodies could accumulate as much as 3000 ppm of base metal and 20,000 ppm of iron as sulphides (Barnes 1988, pages 34-35). This bacterial reduction process certainly alters the isotopic composition of sulphur, though it has not been demonstrated (and is not likely) that the much heavier isotopes of lead can be fractionated by bacterial action.

All these reasons sometimes make impossible the precise dating of ore deposits and rocks by the common lead method alone; on the other hand the processes disturbing slightly the lead isotope composition of minerals from a given ore deposit produce an isotopic signature unique for this deposit which can be measured and used as a lead isotope 'fingerprint'.

4.6. Ore bodies with inhomogeneous lead isotope compositions.

Conformable (strata-bound) ore deposits, together with many for which the geology is not yet completely understood, each have a relatively constant isotopic composition within the particular ore body. In contrast some vein-type ore deposits have revealed the presence of linear arrays of data points in one or both lead isotope diagrams. They may be mixing lines or they may have

the significance of isochrons; their interpretation is discussed by Köppel and Grunenfelder (1979). Such anomalous, or multistage, ore deposits can sometimes present difficulties for archaeological provenance studies. Thus far they have not been found, for instance, amongst Mediterranean ore deposits, but they have figured in studies of galena sources for Archaic/Woodland sites in North America (Farquhar and Fletcher 1984).

Archaeometric research of a Canadian team from Toronto (Farquhar and Fletcher 1980, Farquhar and Fletcher 1984) included the ores of the Upper Mississippi Valley lead-zinc district, whose lead isotope compositions vary over the range of about 3%. It must be emphasized that this variation is for an ore district of about $10,000 km^2$ in area which comprises many individual ore deposits. Surprisingly little detailed work has been done on individual deposits within this district, but the Amelia mine (mentioned earlier) shows only about 0.25% variation in lead isotope composition. Isotopic inhomogeneity on the scale of an ore district does not necessarily preclude lead isotope compositions from pinpointing the source of metal to an individual ore deposit within that district.

On the other hand some of the individual mines within the Mississippi Valley ore district have a large range of variation in isotopic composition. For instance the Buick Mine (Sverjensky 1981) exhibits a range of about $\pm 2\%$ on average in lead isotope composition. Moreover a total variation of lead isotope ratios of about 3% has been demonstrated by ion microprobe analysis in a single crystal of galena from this same Buick Mine (Hart, Shimizu and Sverjensky 1981). However, so far such inhomogeneity is not known amongst the ore deposits exploited in antiquity in Europe and the Near East. Nevertheless, it is important always to know the geological characteristics of each mineral deposit which is considered as a likely source of mineral for ancient artefacts, because the interpretation of the lead isotope data depends crucially on the information concerning the range of lead isotope ratios which might occur in one deposit.

4.7. Other isotopes in geology.

Strontium isotopes are also successfully used in geological dating and it seems that there might be a widening scope for the adaptation of this technique for applications in archaeological science. Strontium is a member of the alkaline earths and is known to replace calcium in many minerals. Therefore strontium is dispersed in all calcium bearing minerals, its salts are dissolved in fresh and sea waters and it is present in sedimentary and igneous rocks. From the soil and water strontium compounds enter the plants, animal and human habitat. Strontium has four naturally occurring isotopes: ^{88}Sr,^{87}Sr,^{86}Sr and ^{84}Sr, all of which are stable (that means that they do not emit natural radioactivity like C^{14} or U and Th isotopes). Their isotopic abundances are approximately 82.53% 7.04%, 9.87% and 0.56% respectively. The isotopic abundances of strontium are variable because of the formation of radiogenic ^{87}Sr through the decay of naturally occurring ^{87}Rb. For this reason the precise isotopic composition of strontium in a rock or mineral that contains rubidium depends on the age and the Rb/Sr ratio of that rock or mineral. Rubidium and strontium are dispersed elements whose concentrations in igneous, sedimentary and metamorphic rocks range from a few parts per million to several hundred parts per million. In isotope archaeology the dating of the rock or mineral is not attempted, instead the characteristic strontium isotope compositions of samples originating from possible sources of raw material used for an archaeological artefact are analysed and compared with the isotope composition of strontium present in the object. Sometimes, it is enough to measure the strontium isotope composition of the archaeological material to relate it directly to a certain, broadly defined source like for example sedimentary rocks of certain age. The variations of the strontium isotope composition of seawater through geological time have been measured by isotope geochemists, by measuring Sr isotope compositions in fossil shells and marine limestones of known age. Figure 11 shows that seawater strontium

exhibits, as a function of time, a maximum variation of about 0.3%, which is approximately 30 times the experimental resolution of 0.01% in measuring isotope ratios of $^{87}Sr/^{86}Sr$. Isotopic measurements are easily made on on as little as 500 ng of strontium.

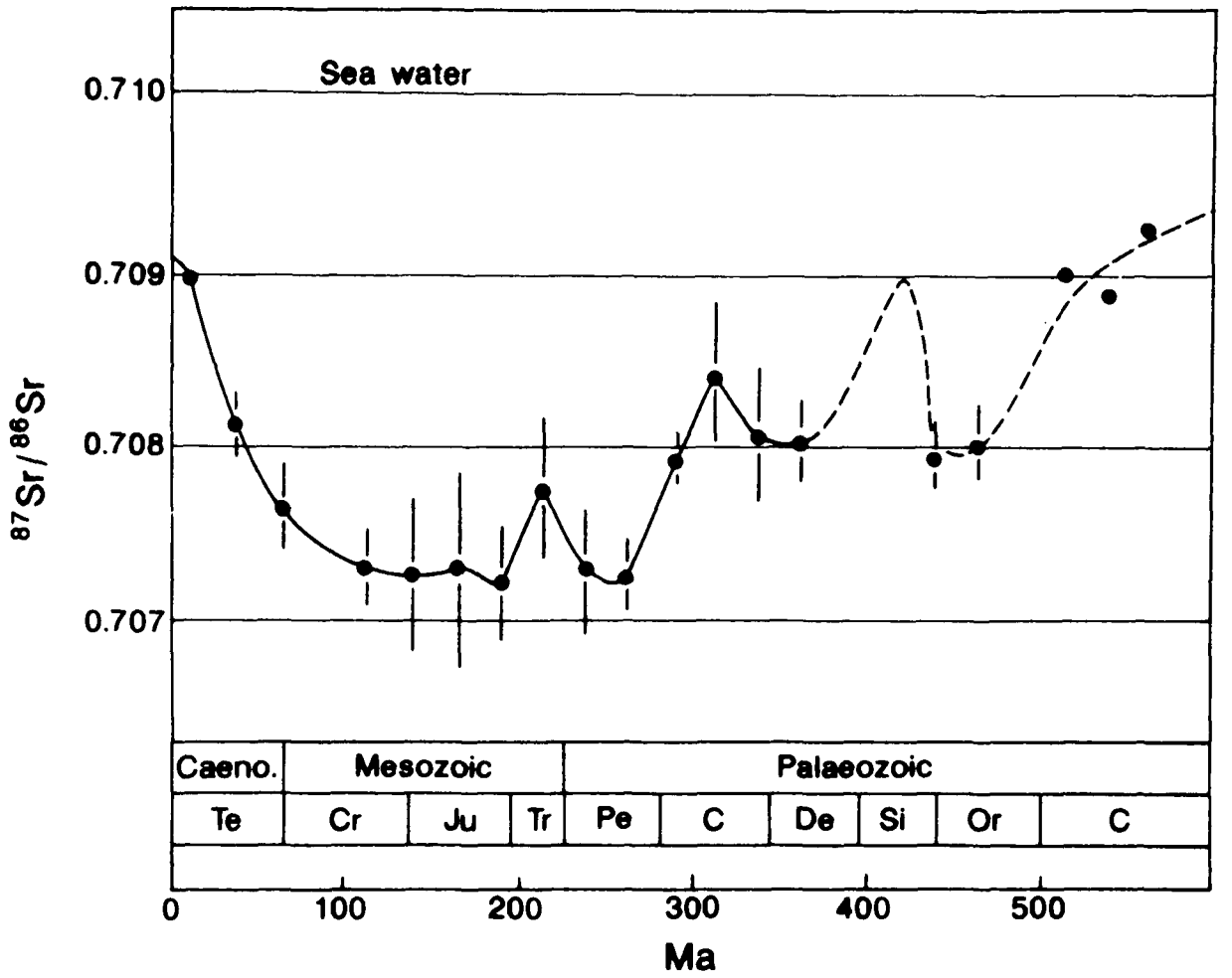


Fig. 11. Strontium isotope compositions of the sea water in different geological periods.

The potential of strontium isotope studies applied to archaeological problems is considerable and can include most materials from natural rocks (for example, marble and gypsum), ivory, bones and others containing calcium and strontium.

5. THE BASIS OF LEAD ISOTOPE FINGERPRINTING OF ANCIENT OBJECTS.

5.1. Minerals and metals in Antiquity.

In the development of civilization, agriculture and mining were the first industries exploiting raw materials. Mining, or perhaps at first just collecting, of minerals by man started perhaps some 30,000 years ago with the search for tool making materials and pigments. Mineral pigments started to be used in cave paintings and pottery decorations. It is known that in ancient Egypt lead sulphide (galena) and copper carbonates (malachite and azurite) were used as cosmetic paints since Predynastic times. Very likely in many other geographical areas colourful minerals had a similar use, as they seem to have done in the Eneolithic sites around Ai Bunar. Perhaps the attempts to purify such pigments, or experiments with burning them, led to the discovery of smelting metals.

Gold was most likely the first metal discovered by man; it occurs in the metallic (native) form in stream-beds and rocks, and could hardly have escaped the attention of a hunter-gatherer. The first metal to be smelted - that is changed from a mineral into the metallic form by the use of fire - was most probably lead, followed around 6,000 BC in the Middle East by copper (Maddin et al. 1991). In Europe the earliest artefacts made of copper, dating to the 5th millenium BC, have been discovered at various sites in Bulgaria, including the immensely rich cemetery near Varna in Bulgaria. Some 1,000 years later a better kind of copper based metal was discovered - arsenical copper - which was smelted from copper ores containing arsenic minerals. During the third millenium BC a superior quality alloy of copper and tin replaced arsenical copper, and that in turn was replaced by iron at the beginning of the first millenium BC. One could argue that metallurgy was the parent of all pyrotechnological developments and in a sense the driving force of our civilization.

Metallurgy has developed in different parts of the world at a different

pace, and the stages of development were not the same everywhere - for example American Indians used native metals to a much larger extent than was ever possible in Europe, Near East or Africa. On the other hand there is no doubt that the earliest and most sophisticated developments in metallurgy took place on the Euro-Asian continent. The development of colouring pigments for pottery, glass, glazes, frescoes and cosmetics is undoubtedly related to metallurgy: the same methods of prospecting for raw materials must have been used, and possibly at times the same ore deposits supplied the minerals. Only a few metals occur in a native form; of those used in the earliest history of mankind only gold was certainly used in its native form until comparatively recent times. Native copper and silver, and also native and meteoritic iron might have been used to a certain extent in the early stages of metallurgical experiments. However, chemical analyses of silver and lead from Predynastic Egypt (3rd millenium B.C.) prove that silver was already at that time extracted from galena (Stos-Gale and Gale 1980). Similarly, analyses of the earliest copper artefacts from Europe and the near East show that only very few of the earliest artefacts might have been hammered out of native metal. There is a growing body of evidence to suggest that smelting of copper was, in some parts of Southwest Asia, being carried out already by the 7th millenium B.C. (Maddin et al. 1980).

The introduction of metallurgy undoubtedly exerted a number of important influences on craft specialization, personal wealth and social hierarchy. The identification of the geographical location of the metal sources used by various cultures in particular times in the past should throw light on the economy of ancient societies, trade routes and inter-cultural contacts. Written historical records are available only quite late in the history of technological development. There is no unambiguous record of metal sources and metal trade in the ancient world for over three millenia before classical Greece. Even Greek and Roman sources highlight only certain aspects of the economy, and much of the informa-

tion on metallurgy is missing. The reconstruction of these early developments can be made only by studies of the metal artefacts - witnesses of that time.

Phot. 2. Each of these pieces of raw copper ingots ('oxhide ingots') excavated at Mycenae contains information about the origin of the metal locked in their lead isotope composition, and about the Late Bronze Age copper technology, reflected in the trace elemental pattern and inclusions in copper metal.

5.2. Geochemical background of metal provenance studies.

For over fifty years attempts have been made to link Bronze Age objects made of silver, lead and copper-base alloys to the ore source through comparative chemical analysis of the objects and known copper sources. These attempts produced many thousands of chemical analyses of ancient artefacts but have failed to trace the sources of the metals. This failure is not unexpected, because the chemical composition of an ore can vary significantly within any ore body and because smelting of ore to produce metal alters the pattern of trace element

concentration as between ore and metal. A successful approach to this problem must depend on a measurable property which passes unchanged through the chemical and metallurgical processes of smelting, casting, forging etc. Such a property is the isotopic composition of lead, for even objects made predominantly of silver, copper or iron, usually contain small quantities of lead derived from the ores.

Table 2. Most common mineral associations of metal ores used in antiquity.

Main metal	Most common associations	By-product in solid solution	Major minerals
Copper	Pb, Fe, As, Zn, Au		Malachite, azurite, chrysocolla, chalcocite, bornite, chalcopyrite
Lead	Zn, Ag, Cu, Bi	Ag, Bi	Galena, cerussite
Tin	Fe		Cassiterite
Zinc	Pb, Cu, Ag	Pb, Cu	Sphalerite, smithsonite, calamine
Gold	Ag, Cu	Ag	Native gold
Silver	Pb, Au, Cu	Au, Pb	Acanthite

Ore consists of useful ore minerals and unwanted gangue. Most ores contain several associated recoverable metals; very often one metal is present in several different mineral forms. Table 2 presents the most common associations in ores of metals used in antiquity (loosely based on Barnes 1988, p.14, Table 2.1.). The primitive metallurgical processes often resulted in high levels of metals from associated ores remaining in the chiefly sought metal. Therefore, copper smelted in the Early Bronze Age usually contains various concentrations

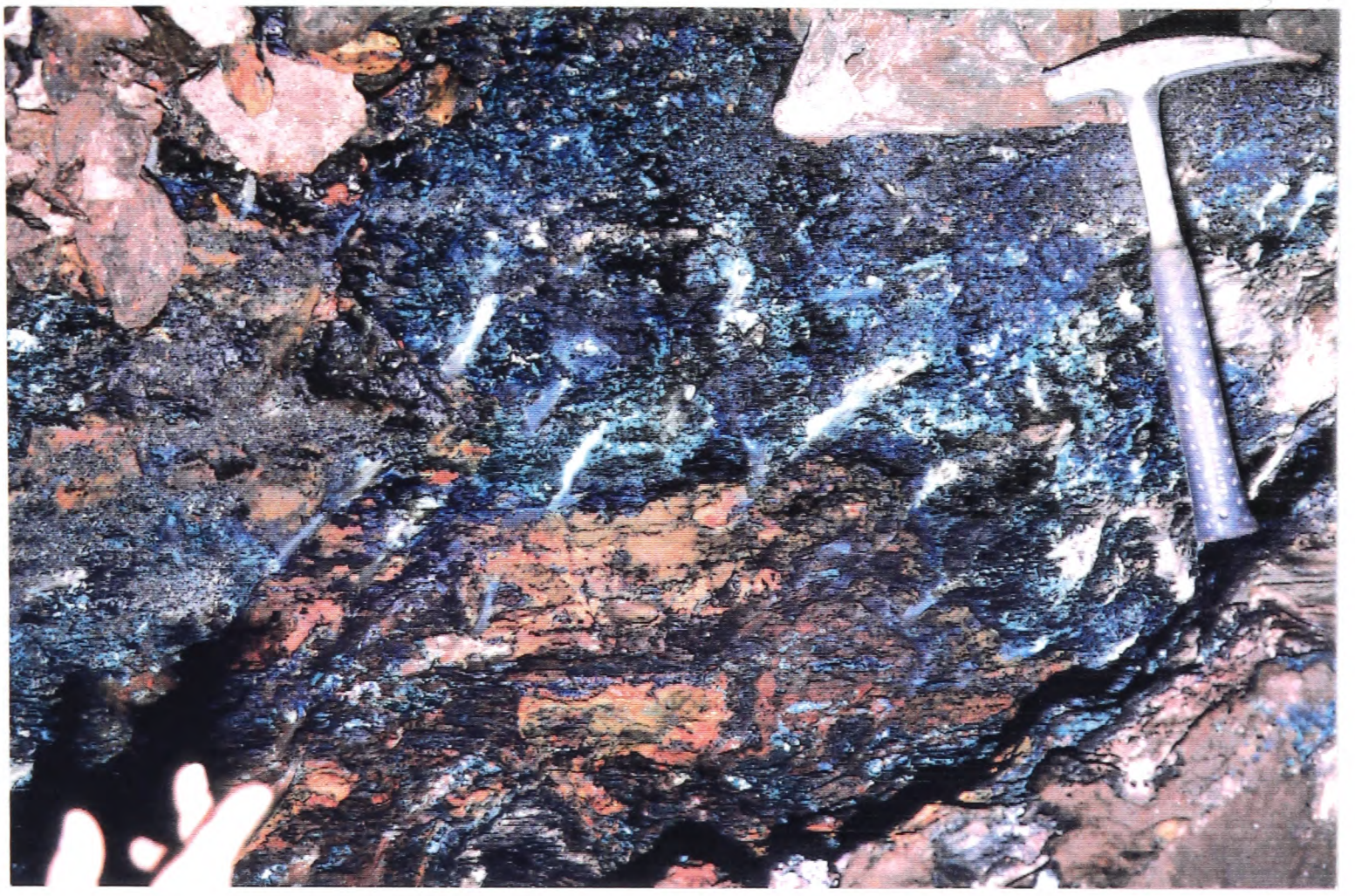
(sometimes even several percent!) of lead, iron, nickel, cobalt, zinc, arsenic and antimony. Lead is most commonly associated with silver, copper, iron and zinc minerals. All those, together with lead itself, are the metals which played a major role in the development of metallurgy. The most common ore minerals which can be readily smelted in primitive conditions are carbonates, oxides and sulphides. The most important lead mineral is the lead sulphide - galena (PbS); rich copper sulphides include chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4). Many sulphides contain other sulphides in solid solution. Thus copper sulphides always contain traces of lead. On the other hand galena commonly contains varying quantities of silver sulphide, argentite (Ag_2S), with bismuthinite (Bi_2S_3).

Galena has a quite remarkable appearance - silver coloured, heavy and 'metallic' looking, it might have been one of the first minerals which attracted the attention of man. Likewise, two most strikingly coloured basic copper carbonates: bright green malachite ($CuCO_3.Cu(OH)_2$) and blue azurite ($2CuCO_3.Cu(OH)_2$), were most likely the first copper ores to be smelted to metal.

In one ore body all elements have basically the same geochemical origin from the time of the ore formation. Some secondary minerals are formed due to the erosion of the ore body, therefore primary lead sulfide (galena) and secondary lead carbonate (cerussite), will contain the same lead with the same lead isotope composition. Likewise all lead disseminated in the ore body, and present in various chemical forms in other minerals, will be the same lead, with the same isotopic composition. Numerous measurements of different minerals from the same deposit prove that there is no isotope fractionation during the weathering and oxidation processes. The differentiation of lead isotope composition within one ore body can be caused only by different ore forming processes; all minerals with the same geological history have practically the same lead isotope ratios,

independent on their chemical composition.

Phot. 3. Copper mineralisation in the galleries of Kamareza mine in Lavrion (Greece).



The lead isotope composition of lead metal was used for the first time as a 'fingerprint' of its origin by Brill and Wampler (1965). In their article, the authors suggested, that since the lead deposits in different parts of the world were formed at different times, then also the isotope composition of lead metal should reflect the geological ages of the ore from which it was smelted. This principle was used for the first time by Brill and his colleagues (1965), and independently by Houtermans and his colleagues (Grogler et al.1966), to identify the origin of some ancient lead objects. In the last twenty years lead isotope provenance studies broadened to include glass (Brill 1968), silver coins (Gale et al. 1980), copper (Gale and Stos-Gale 1982), iron (Gale et al. 1987), painter's pigments (Keisch 1970) and other materials like for example lead in bones (Molleson et al. 1986).

5.3. The principles of the application of the 'common lead' method in provenance studies of ancient objects.

Characteristic lead isotope ratios of ore deposits are different, because the final isotopic compositions depend not only on the age of the ore and the concentration of lead 204 in the primary minerals, but also on the concentrations of the parent isotopes, uranium and thorium, and possible remobilization of the ore. On the other hand within an ore body of the same origin the lead isotope composition should be the same for all minerals. Specific isotopic compositions are imparted to the mineralization during the transport and deposition of the metals from hydrothermal solutions (Gulson 1986). In the course of these processes the lead isotope compositions will be homogenized. Following deposition, this characteristic composition may be altered due to the decay of any U and Th still present in the ore. For high lead deposits this effect is minimal, but in low lead minerals the change might be noticeable. If there is a significant difference in the U and Th content in different parts of the ore body, then the signatures of minerals from the different parts of the same deposit may be different, but this is not common. So far only lead isotope 'fingerprints' of two well known copper deposits in the Near East, Feinan and Timna, show this effect. However, good geological and archaeometallurgical knowledge of these mines allows succesful use of their lead isotope compositions in the provenance studies (Hauptman et al. 1992).

The inhomogeneity of the distribution of uranium and thorium in the Earth's crust before ore formation, and subsequently the separation of lead from the parent isotopes during the formation of the deposit, introduces random variations into the lead isotope composition. If we look at a specific unit on the earth, then we have to consider it as a system which was open during all processes leading to the final ore formation. For this reason one can expect much greater variation in the lead isotope ratios of terrestrial minerals than if

they were dependent only on the geological age of the formation, as discussed in Chapter 4.

The change of ^{206}Pb and ^{238}U, for example, was described by Allegre and Michard (1973) by the following expression:

$$\frac{d^{206}Pb}{dt} = \frac{d^{238}U}{dt} - L(t)(^{206}Pb) + G(t) \tag{5.1}$$

where $L(t)$ is a rate of loss of ^{206}Pb and $G(t)$ is a gain of ^{206}Pb from outside sources.

It is possible also that the concentration of ^{238}U will not only be diminished by radioactive decay, but also might be increased by gain from outside sources. In principle therefore, minerals of different geographical origin have a high probability of displaying not only different, but also uniform and characteristic within each deposit lead isotope compositions. Lead isotope provenance studies, should allow, in an ideal case, the identification of a geographical source of lead present in an ancient artefact, by comparing its lead isotope composition with lead isotope compositions measured for mineral deposits. This comparative method requires availability of lead isotope data for ore deposits which might have supplied the mineral. Until now this aspect of the lead isotope provenance studies was largely ignored. Many research projects have produced numerous lead isotope data for archaeological artefacts, which cannot be interpreted for lack of an appropriate database for the ore deposits (Collin 1990, for example). On the other hand, even without the final association of the object with an ore deposit, lead isotope 'fingerprints' of artefacts can provide some other useful information: for example they can highlight similarities or differences of origin between the artefacts, or exclude the possibility of an object originating from a known ore deposit.

It was mentioned in the previous chapters, that due to the mixing of the

ore-forming fluids, the lead isotope compositions of all ores in one mineral formation are usually quite homogeneous, and cover only small ranges of values measured for the three independent lead isotope ratios. In theory, of course, these characteristic ratios can be fairly similar, or even identical, in geographically distant ore deposits. To a certain degree, such a possibility can be estimated on the grounds of their geological dating, determined either by isotopic or other geological methods. However, since there are many, largely unknown, factors which might have influenced the lead isotope 'signature' of an ore deposit prior and after its formation, it is not possible to assess its exact value, or extent from the geological age. At present the only way to characterise accurately the lead isotope composition of any possible source of metal is to analyse many different minerals from different strata and distant parts of a deposit. The geology of the deposit must be taken into account at all times.

So far, archaeological lead isotope studies have had the greatest impact in the field of archaeometallurgy. The lead isotope composition, unlike the chemical composition, does not change during metallurgical processes - therefore the ore, slag and metal produced from a given ore deposit all have the same, unchanged, lead isotope fingerprint. Results of laboratory experiments proving this point were published by Barnes and his colleagues in 1978. Since then many analyses at Oxford of ore, slag and metal from archaeologically dated smelting sites on Cyprus (unpublished data), Kythnos (Stos-Gale 1989) and other sites, have confirmed and strengthened this conclusion. Lead isotope 'fingerprints' are so far the only measurable characteristics of the chain: *ore-slag-metal*, which allow provenancing to be achieved. The use of lead isotope analyses on all these three types of material allows the identification of a deposit from which the ore was brought for smelting and to trace the further distribution of metal produced from this ore deposit, or on a particular smelting site.

5.4. Methodology of the archaeometallurgical lead isotope provenance studies.

Provenance studies by the lead isotope method can draw only to a certain extend on geochronological research. In general, geological prospectors and geochronologists are not concerned with large, well known copper or lead deposits in the old world. Most of the lead isotope data of ore minerals published in the last decade in geological journals was collected to characterise the North American and Australian mineral deposits. Much of the data published by isotope geochemists is that of country rocks, or specific rock formations. All this information is quite useless for archaeometallurgy. Archaeometallurgical research into sources of metals used in antiquity must be combined with field expeditions collecting mineral samples for chemical and isotopic analyses. In an ideal case each ore deposit which might have been used in ancient times should be characterised geologically and mineralogically and provide a selection of at least 20 lead isotope analyses of different minerals relevant to metallurgical activities.

The number of ore deposits in Europe and the Near East is quite limited and moreover, many ancient mines and metal smelting sites are already known, either from literary and mining sources, or from archaeometallurgical field work. Figures 12 a and b show geographical positions of European ore deposits which might have been of importance for ancient metallurgy. So far, there is no comprehensive publication covering all presently available evidence of the ancient exploitation of the mineral deposits in Europe. It is very likely that most (or even all) of the largest mineral occurrences were used in the past.

Ideally, in parallel with sample-collecting activity, examination of such deposits for signs of ancient mining should be carried out. In our work in the Mediterranean, which successfully proved Bronze Age exploitation of several unexpected deposits (for example copper in Lavrion; Gale and Stos-Gale 1982

Fig.12a. European ore deposits important for archaeometallurgy.

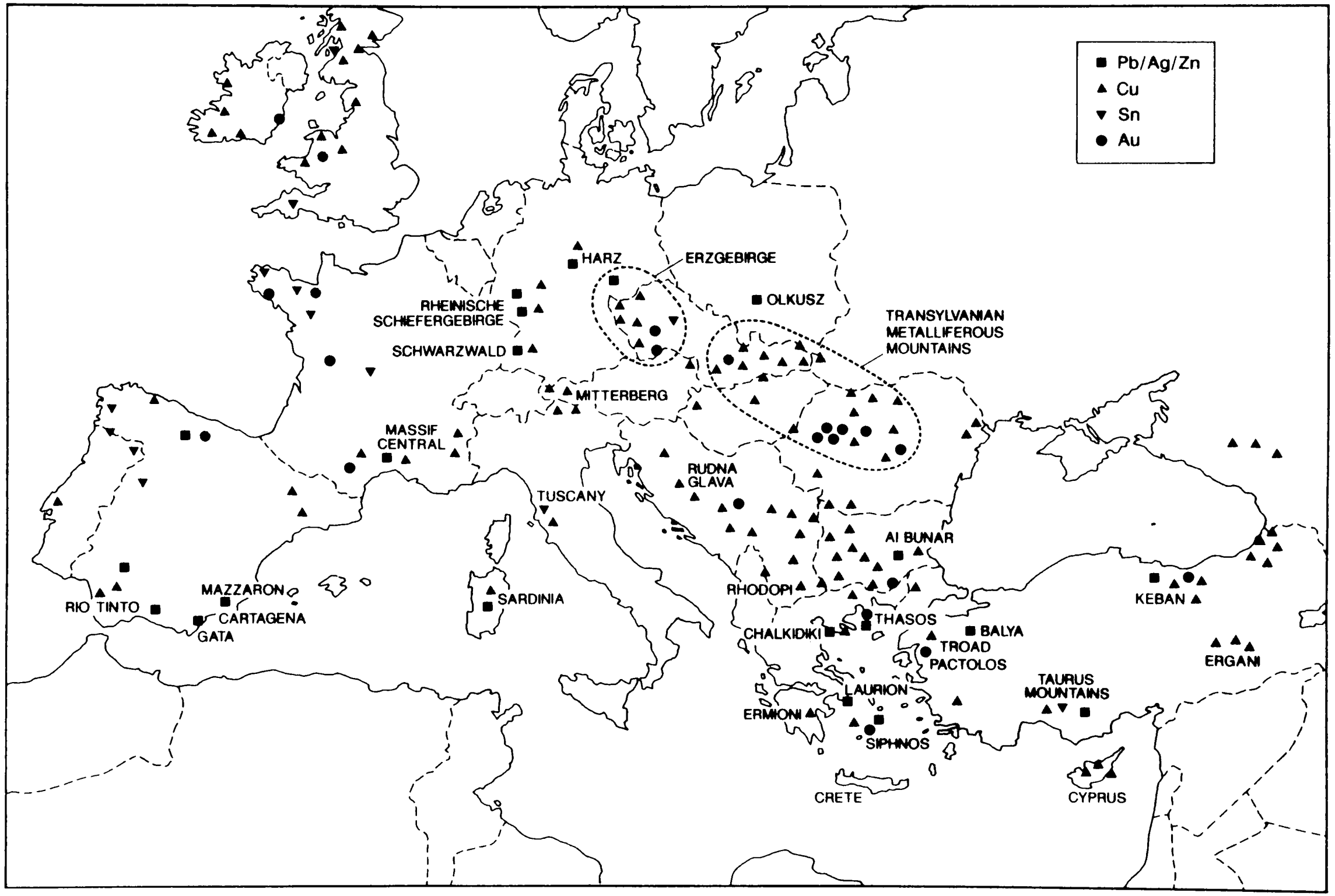
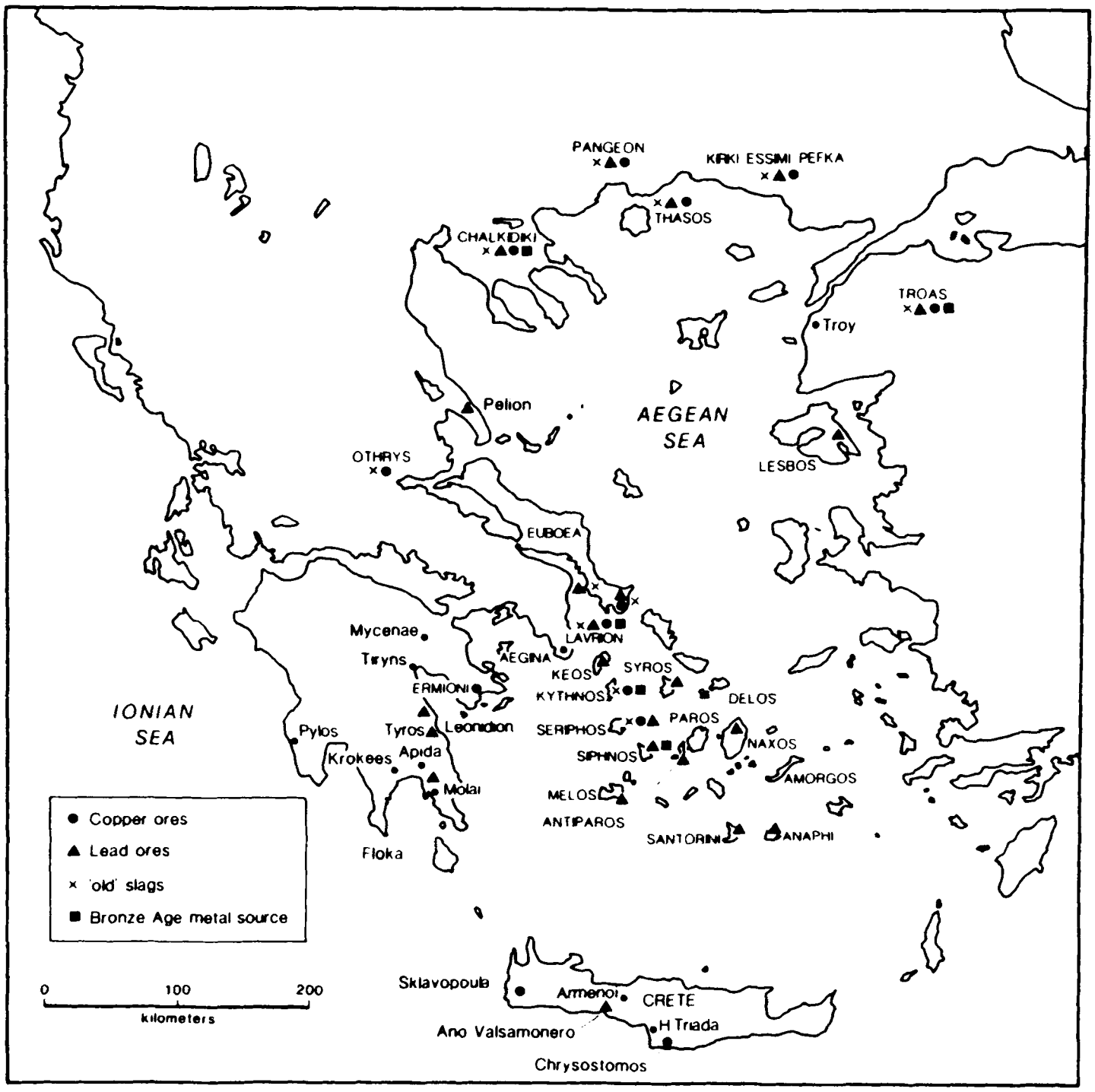


Fig. 12b. Ore deposits in Greece.



and Kythnos; Stos-Gale 1989). The research before each fieldwork trip consisted of reading various ancient and more recent descriptions of metal deposits (for example, Davies 1935, Fiedler 1841, as well as Agricola, Strabo and Pliny). The modern geological literature is of limited value, because the economic geology of our times often neglects resources which might have been of great importance in antiquity. On the other hand the mining journals and books of the 19th century are of great utility, because quite often the mines which were started then, followed earlier mining, and there are descriptions of old shafts and galleries. The metallogenetic maps of the areas relevant to a given research are very useful, but the best approach is through collaboration with local geologists, who know the area. In many parts of Greece, for example, the maps are often of little use because of their inaccuracy and the wilderness of the terrain. Most of our information about the Greek, Cypriot and Italian ore sources was accumulated only thanks to the help of local geologists and people living in the vicinity of the mines and smelting sites. On the other hand, in highly industrialized countries like Britain or Germany, such work is much more difficult. The major metal deposits are often either totally exhausted, in which process all traces of earlier activities, and even minerals, have been altogether obliterated, or the mines are still active and the access for archaeometallurgical studies is difficult. In both cases, however it should be possible to accumulate enough samples of ores, perhaps from the mining company, the local mining museum or private miners' collections, to assess the range of minerals occurring in the deposit and measure their lead isotope composition. On such occasions the lead isotope characterisation of the small amounts of ore still to be found there, might result in finding the only reliable proof of the exploitation of the deposit in antiquity, and date it by providing a link with dated ancient metal artefacts.

Much of this sort of work has been carried out in the recent decade in the Mediterranean by our group and the German team from the Max-Planck

Institut (Mainz and Heidelberg). The German team produced very good geological descriptions of many Turkish copper and lead/silver deposits (Wagner et al. 1989 and references within), but very few lead isotope data of relevant ores have been published so far (55 mostly single analyses from nearly 200 sites). Some more data for the deposits in the Taurus Mountains in southern Turkey have been published recently by Yener et al. (1991). At present most of the lead isotope data for the Mediterranean ore deposits comes from Oxford. There is very little similar work done in other parts of Europe. There are well known ancient mines in Austria in Mitterberg, and others in Germany, for which there is little lead isotope data as yet published. Some work is being done at present at Oxford on the isotopic characterization of the important Balkan copper deposits of Ai Bunar (and other Bulgarian occurrences), and in Mainz on Rudna Glava in Serbia. Recently, a SERC supported student at Oxford began lead isotope research for the Bronze Age metallurgy of British Isles. Some of the lead isotope data published in geological and geochronological literature also can be used for archaeometallurgical interpretation, but unfortunately geologists usually analyse only a small number of samples from one mineral occurrence.

On present evidence, it seems that a large number of highly accurate lead isotope analyses of relevant (mainly copper, silver and lead) ore samples for characterization of one ore deposit are of crucial importance for provenance studies. Accurate analyses of ore samples provide the vital information needed to establish the exact size of the lead isotope field for a given deposit and to aid the discrimination between different deposits as much as possible. There is no widely accepted theory which would specify the maximum range of lead isotope ratios possible in one mono-geochronological deposit. Begemann (et al. 1989) concluded that the range of lead isotope ratios in one deposit is in fact identical and in practice equal to the analytical error of 0.1% (this statement was based on analyses of just a few samples). Our lead isotope analyses of a

variety of minerals from the same deposit show that this is a serious underestimate (the experimental data are discussed in Chapter 6). In fact there is always a certain range of lead isotope ratios in one deposit (a theoretical discussion is presented in Chapter 4). The slight differences in the lead isotope compositions within one mineral deposit are very likely to be connected with the initial slight inhomogeneity of the distribution of U and Th and lead in the ore forming fluid. Some ore deposits studied by geologists (usually those really big lead/zinc sulphide deposits of Northern America and Australia) have a large range of lead isotope ratios and then only a very careful scan throughout the deposit can provide its real lead isotope 'fingerprint.' The deposits relevant to the archaeometallurgical work in Europe have largely not been investigated by geologists from the point of view of their lead isotope range. From analyses collected for this work it seems that the range of lead isotope ratios within one ore deposit is usually slightly below 0.5%, though, if more than 10 samples are analysed the range is nearly always larger than the analytical error of 0.1% (See Table 4 in Chapter 6). However, the recent statement by Knapp (1991) that more analyses largely increase the range of lead isotope ratios for a given ore deposit does not find any confirmation either in theory, or amongst the experimental data. If all the lead isotope ratios for a mineralisation are measured with high accuracy, then their range depends more on the choice of samples, rather then their number. For example, 50 analyses of galena from one mining waste-heap, where ore from the same vein was dumped, might result in a smaller range of lead isotope compositions than 6 samples from 6 different dumps in the same locality. Naturally, the exact range of the isotopic 'fingerprint' varies from deposit to deposit, but it is quite clear from the geophysical and geochemical processes governing the variation of lead isotope compositions in minerals, that only a very limited range of lead isotope ratios is possible in minerals with common geological history.

Another important condition (apart from a satisfactory number of mineral samples) for establishing the real range of lead isotope ratios for one ore formation, is the high accuracy of isotope measurement (at least $\pm 0.1\%$). The inclusion of poor data in the 'fingerprints' of ore deposits impedes in particular all statistical evaluation of the data. In the last year we had to repeat many old measurements of ore samples from Cyprus and Lavrion to check the exact ratios of these samples, because scientists in the Smithsonian, using statistical methods of evaluation of our data, were arguing for geological 'outliers' (Sayre et al. 1992), that is samples of ores with lead isotope ratios far removed from the bulk of ores from a given deposit. The inspection of old laboratory records and repeated analyses of the same ore samples, proved that some of the old data were of poor accuracy, and that the 'outliers' were not real. All inaccurately measured data will confuse comparisons between the ore sources and ancient artefacts, because many fingerprints of ore sources used in ancient Greece, for example, are different in their mean values only by tenths of a percent, and therefore it is very important to establish the exact position of the lead isotope ratios of each artefact in relation to the ore measurements. For this reason only thermal ionization mass spectrometry at present guarantees good results in provenance studies. Other methods of isotope measurements, including inductively coupled plasma quadrupole mass spectrometers, and solid source ion-gun ionization cannot as yet guarantee sufficiently accurate measurements.

5.5. Complications in finding the true origin of metal.

Provenancing using lead isotope analyses is simple in principle, involving just comparative measurements of lead isotope artefacts and ore deposits and the search for matches of composition. However, the conclusions drawn from such comparisons are only true if the metal originates from a single ore source. In contrast with marble, obsidian or pottery, metal is in principle susceptible to mixing and remelting. It is obvious that in the case of mixing of two or

more of three-dimensional lead isotope signatures, the outcome will represent a new one with the values of lead isotope ratios somewhere in between. The final values will depend on the amount of each metal taken for alloying and on the amount of lead present in each of the parts used. One can imagine that 'mixing' of several different 'fingerprints' will result in a scatter of points, over a wide range of lead isotope ratios, which can fall at random into lead isotope fields of ore sources without really originating from them. For this reason lead isotope provenance studies of metal alloys are usually limited to cases where one can reasonably assume that there was no widely employed recycling of metal from a diversity of sources. However it seems likely, that for a large part of human history, the major metal supplies for particular areas were really not as diverse as is often imagined. Only a careful examination of lead isotope ratios of metals from different parts of the world and different periods, backed up by a wide database of the relevant ore deposits, can answer the question of how prevalent was mixing of metals.

Another problem is presented by lead introduced to the final metal from the components of the alloy which might be added separately (for example tin or lead to copper). Arsenical copper was perhaps the earliest alloy in the sense of production of metal which consisted of two major components. This process, however, was done most likely by smelting together copper ores mixed naturally with arsenic minerals (for discussion see Merkel et al. 1992). In this case arsenic and copper minerals were of the same geological origin and therefore the same lead isotope composition. Chronologically, the next type of alloy is tin bronze. Tin bronze is the first example of the widely employed deliberate alloying of two metals of quite different origin, because a great majority of the European and Near Eastern copper deposits do not contain tin minerals. The mineral which almost certainly was used in the Bronze Age for production of tin metal is cassiterite (SnO_2). If lead were present in cassiterite then the lead isotope

composition of the copper ore in a bronze artefact would be quite disturbed. The only published analyses of cassiterite, which includes lead amongst other elements, are those of Taylor (1979). The analyses of cassiterite show that, for six of seven geological classes of cassiterite deposit, the mean lead content is less than 50 ppm; only in the quartz-sulphide type occurrence does the mean lead content rise to 130 ppm. These data suggest that even for very high tin bronzes containing 20% of tin, the cassiterite would contribute on average only about 10 to 26 ppm of lead to the bronze. Copper ores usually contain much higher concentrations of lead and most of the ancient metals have lead contents between 0.1% and 2%.

What then if lead is added deliberately? The elemental analyses of several thousands of Bronze Age Mediterranean artefacts analysed in our laboratory and many other published data (for example Craddock 1976) prove that deliberate alloying with lead was not practiced in the Mediterranean and the Near East until the first millenium BC. It seems that in the copper based artefacts from the Bronze Age any excessive amount of lead comes most likely from the mixed copper/lead ores used for smelting of copper (Stos-Gale 1992a). It has been attested that, even with relatively sophisticated 19th century technology, the presence of lead minerals mixed with copper ores can result in copper containing even as much as 20% of lead. Percy (1890, p. 306-307) gives chemical analyses of black copper from Freiberg in Saxony, all analysed samples contain zinc, lead and iron; one of them had 20.75%of lead, 3% of iron and 0.91% of zinc. Also, other analyses of black copper smelted from European ores (Percy 1861, p.408, 422, 429 and 503) show consistently up to 3% of lead. Many European ore deposits are multimetallic, that means minerals of various metals occuring side by side, or even mixed together and, depending on the choice of the mineral for smelting and the technology, production of copper metal from such ores can result in copper containing varying amounts of lead, as well as other elements. In fact

many metallurgical technologies in the last few hundred years were developed specifically for purification of smelted metal. There is no evidence that in the earliest days of metallurgy (at least until the Roman times) there were any such purification processes employed. In that case the purity of smelted metal would depend mostly on the choice of rich ore and its pre-selection and concentration. The elemental composition of an alloy of an archaeological artefact is a very important factor in the interpretation of lead isotope data and should be known in advance of the isotope analysis. If the amount of lead is very high then there is always the possibility that the lead was separately added and such an eventuality should be reflected in the interpretation of the results.

6. THE INTERPRETATION OF LEAD ISOTOPE DATA.

6.1. Critical review of the major publications in the field of lead isotope provenance studies.

As can be seen from the previous chapter, finding the origin of ancient artefacts using lead isotopes is in principle quite straightforward. Lead isotope provenance studies rely chiefly on direct comparisons of the measured 'fingerprints' of ore deposits and artefacts, and in this respect differ strongly from the interpretation of lead isotope data in research concerned with geochronology and geological prospection. However, the possibilities of comparison and interpretation rely completely on the available range of comparable lead isotope data and a proper understanding of the lead isotope characteristics of ore deposits. The research into the Mediterranean Bronze Age ore sources, conducted in Oxford since the early nineteen-eighties, was from the beginning centered on extensive geological fieldwork and a thorough assessment of the metallurgical and archaeological information. The ore deposits were scanned one by one and gradually we are assembling a lead isotope 'map' of this part of Europe, with full information on the type of deposits, minerals occurring there and any signs of ancient exploitation. This approach brings successful results and some of them have already changed archaeological concepts, for example the import of copper oxhide ingots to Sardinia from Cyprus (Gale and Stos-Gale 1987).

On the other hand, lack of the relevant ore data, and a rather superficial approach to the interpretation of the lead isotope analyses of ancient artefacts, can effectively diminish the power of this technique. Many publications in recent years have led some archaeologists to believe that there are severe limitations in lead isotope provenance studies, bordering on the method being almost useless (Muhly 1983, Begemann et al. 1989, Pernicka et al. 1990, Muhly 1991, Knapp 1991). The lead isotope technique requires an understanding of geology, archaeology, chemistry and physics; all too often some of these four aspects are

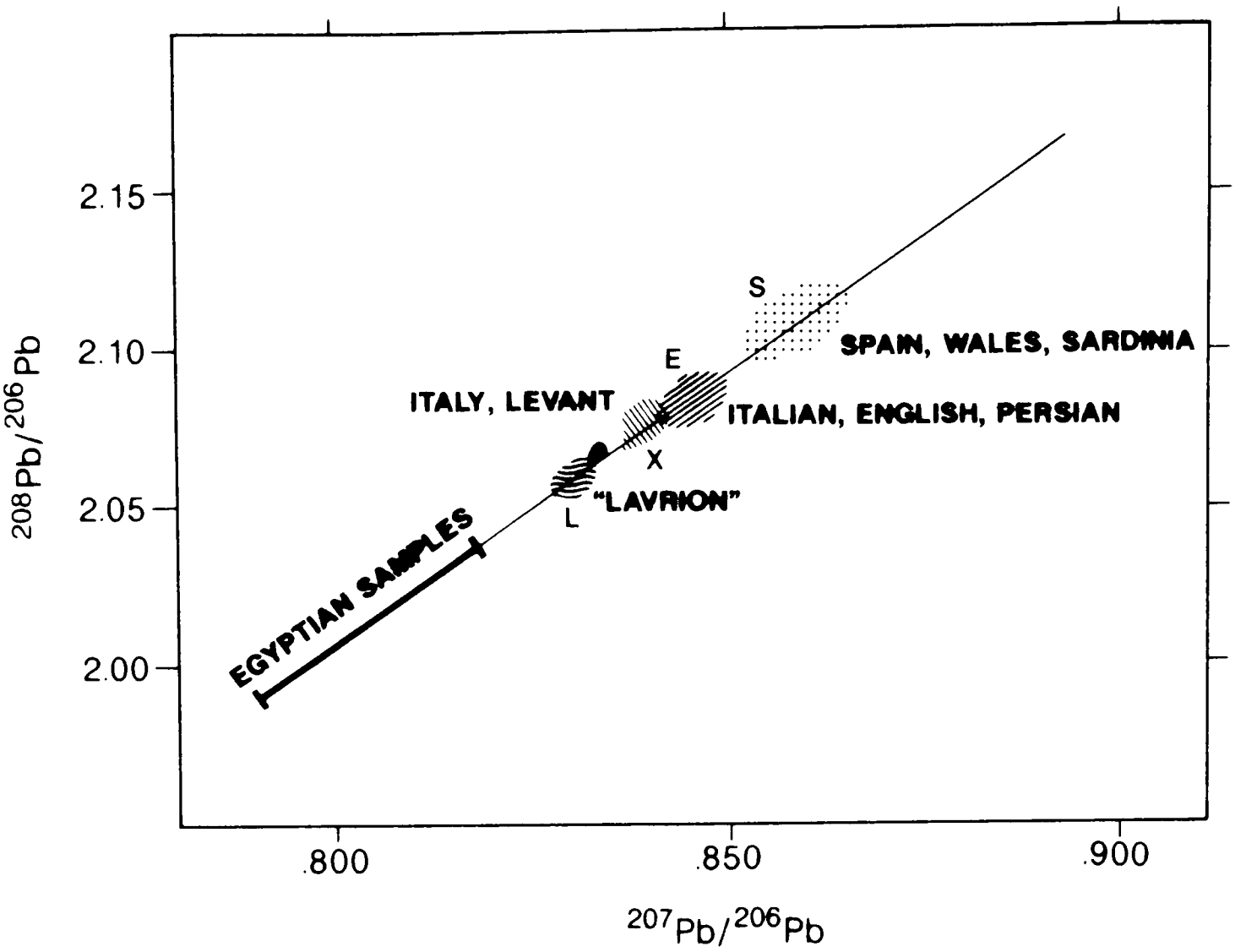


Fig. 13. Brill's interpretation of the lead isotope data of many different ore samples and various ancient artefacts.

lacking, resulting in a thoroughly unsatisfactory discussion of the results.

For example, the method of comparison and interpretation of lead isotope data introduced and used by Brill and illustrated in Figure 13, was adapted from one of his recent papers (Brill et al. 1988), and shows many typical shortcomings in the approach to lead isotope provenance research. For example, the diagram is constructed from the data obtained for some 400 specimens of various archaeological materials and ores from all over the ancient world. For an interpretation of analyses of new artefacts (glasses), matches were sought with the regions of isotopic composition shown on the diagram, labelled L, X, E, S, etc. The groups are vaguely described in the text as: "... L represents Laurion-like leads while group E contains leads from England and Europe ...". These extremely broad lead isotope fields depend on both, ores and artefacts, from all over the ancient

world and are labelled merely according to the geographical origin of most of the ores or artefacts within a given field. They are not geologically and geographically coherent groups and therefore descriptions of the 'fields' are at best misleading. For example, the range of lead isotope compositions of lead and copper ores on Sardinia and in Spain (group S is Spain, Sardinia and Wales!) is far beyond that indicated on the diagram. Descriptions like 'Levant' or 'English, Italian, Persian' are far too general and do not mean anything in terms of real ore deposits, or even groups of artefacts, because if the field named 'Italy' includes artefacts which were in fact imported from Greece, then the 'signature' of a Greek ore is used as part of the field referred to as Italian.

Further, in many cases there is only one analysis of an ore from each deposit, so the extent of the field of isotopic compositions for a given ore deposit remains unknown. The ore analyses used by Brill to construct fields on Figure 13 are almost solely of lead ores from deposits which do not contain copper, yet the artefacts include, for instance, copper-tin alloys which cannot possibly have been derived from such ore deposits. Additionally, the artefacts include glasses, glazes, pigments, bronzes, lead metal and debased silver from the Bronze Age to Roman times from all over the ancient world, and there seems to be little reason for any groupings amongst them. Even the field labelled Lavrion includes ores and objects having nothing to do with that famous ore deposit in Attica, upon which the wealth of ancient Athens depended. The true Lavrion field based on over 100 lead isotope analyses of ores is in fact considerably more restricted. The vast scale of the diagram reproduced as Figure 13, which covers practically all known lead isotope compositions of ore deposits in Europe, Northern Africa and Turkey, obscures completely any discrete differences which might have existed within the marked 'fields'. If the chief purpose of this diagram was to emphasize the difference between the lead isotope composition of Egyptian glass and other ore deposits, then again the comparison is meaningless, because, for example in

Turkey, there are ores of compositions matching the Egyptian samples marked on the two dimensional diagram reproduced as Figure 13. The final, and most important problem with these comparisons is the use of only two of the available three lead isotope ratios. This approach derives from the geochronological interpretation of the lead isotope data, where, in terms of the age, two lead isotope ratios are quite sufficient for calculations. This is not so in lead isotope provenance studies, where the third ratio provides a dimension which can change significantly the interpretation of the data.

Though this approach was perhaps natural in the early days when few isotopic analyses were available (see Brill et al. 1974), it seems unfortunate for it still to be in use in an important publication. The right approach to this study should include only comparisons with the 'fingerprints' of mineral deposits and ancient artefacts which are archaeologically related to Egyptian and Near Eastern glasses. The random use of **any** available lead isotope data obscures the real answers and creates many doubts as to the reliability of the lead isotope technique. Progress can come only from the laborious construction of lead isotope fields for ore deposits in the geographical region of interest and by the comparison of like with like: copper artefacts with copper deposits, lead/silver artefacts with lead/silver ore deposits, etc. Fieldwork is therefore essential, not only to collect ores from known geological horizons for isotopic analysis but also to establish the exact character of the mineral assemblages in particular ore deposits, and to differentiate between ore deposits and mere mineral occurrences (often of thin powdery covers less than a millimeter thick) which can never have been used at any period.

An example of an unnecessarily restrictive use of the lead isotope data comes from a range of publications of the Mainz-Heidelberg group. In one of their most recent papers (Pernicka et al., 1990, p. 282-283) they express a most pessimistic opinion that the lead isotope compositions of lead in ore deposits

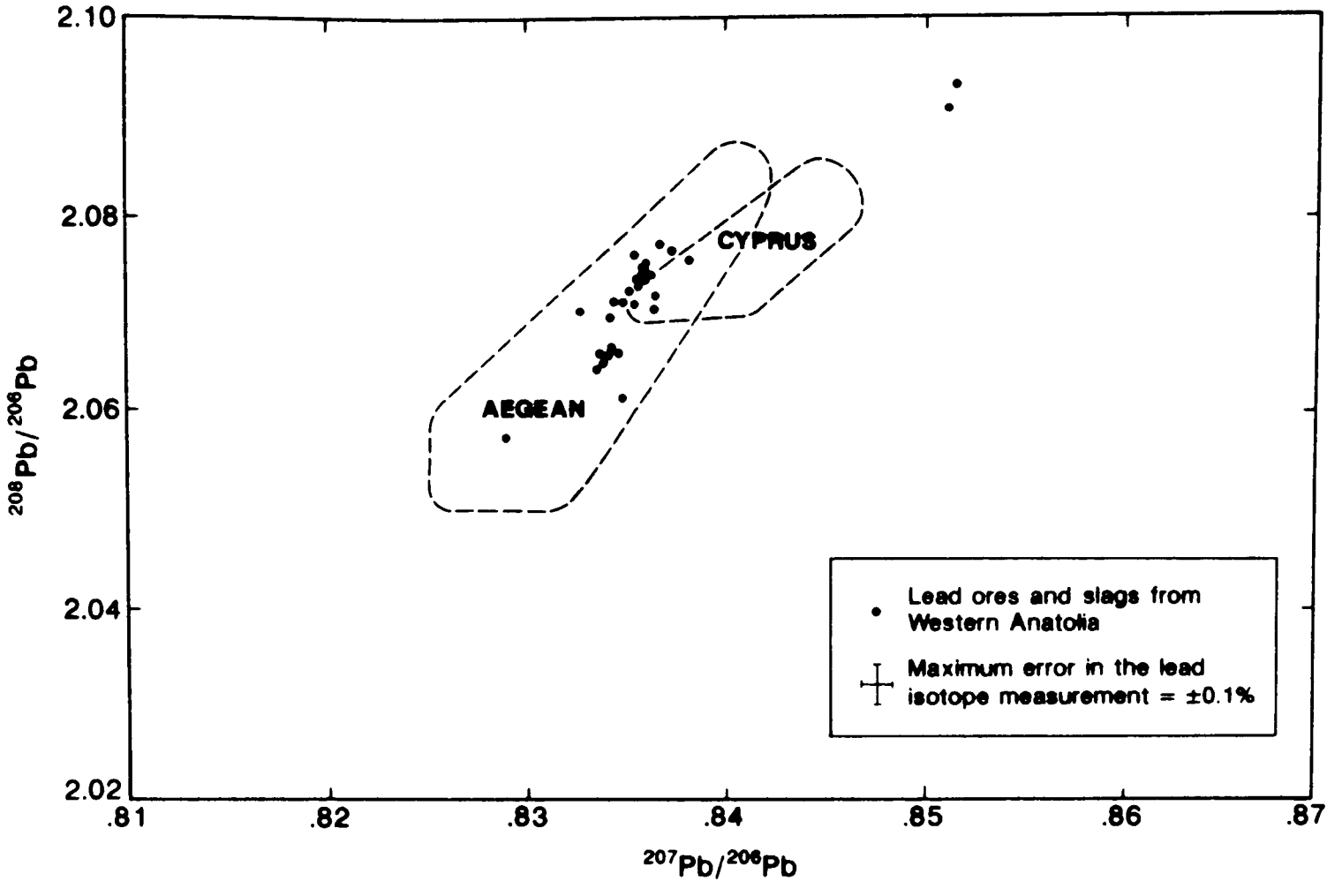


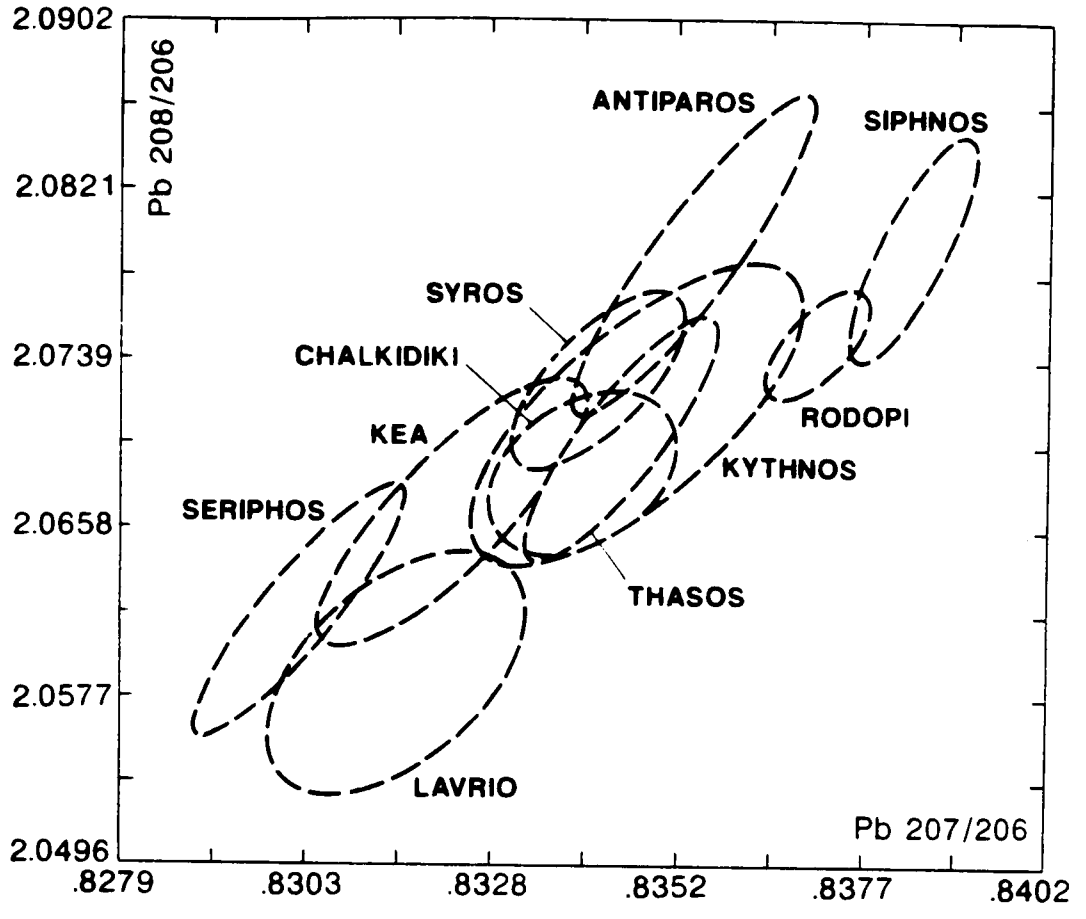
Fig. 14. The bivariate plot of the Aegean and Cyprus fields used by the Heidelberg -Mainz Group for the interpretation of their lead isotope data.

are usually not unique, so that an assignment of an artefact to a single ore deposit is not possible. Their pessimism springs chiefly from limiting the lead isotope analyses of ores, which they collect during very well organised fieldwork expeditions, to just a few samples (often only one) from one deposit. Then the data analysis is limited mostly to the construction of one bivariate plot of the measured lead isotope ratios. Again, this approach is based chiefly on the experience in geochronology. The lead isotope data seems to be treated not as a characteristic set of compositions which represent a comparative **group**, but as if the age of the deposit was sought. In some cases the geochronological instinct leads the scientists as far as to calculate the ages of the ores, even if the authors conclude that the ages have no relevance to the subject of the paper and possibly no geological reality (for example, Hauptman et al. 1992, 19-20).

In the past much of our preliminary lead isotope data published in the

early nineteen-eighties was used by the Heidelberg/Mainz group to construct an 'Aegean lead isotope field' (see Figure 14 adapted from Figure 28 of Pernicka et al. 1984), which was later used for comparison with the artefacts - lead and copper alike. On Figure 14 there are also plotted lead isotope ratios of 'Turkish ores and slags' measured in Mainz. At first sight, this picture gives absolutely no hope for lead isotope provenance studies. However, two bivariate plots of the data reveal that this large 'field' has a visible infrastructure. Figure 15 shows that particular deposits separate into areas of a very limited size, and in fact each of the deposits occupies only a very small, and strictly limited, fraction of the huge area identified by Pernicka et al. A closer examination of the two plots on Figure 15 shows that many of the deposits have distinctly different lead isotope 'fingerprints' when all three ratios are taken into account (Seriphos, Kea, Lavrion, Siphnos, Rhodopi). Many of these in the central part of the diagram do at first sight appear to overlap to a certain degree, but their statistical separation is quite easy and it will be discussed in a later part of this chapter. Another important feature of these overlapping deposits is their geological character: the islands of Syros and Antiparos have only small occurrences of galena and there are no copper mineralisations on these islands. Further, the Kythnos field is constructed from measurements of lead isotope compositions of copper ores and slags found on this island and there are no lead ores of such lead isotope ratios on Kythnos. Thasos and Chalkidiki are in the northern part of Greece and in both locations copper and lead/silver ores are found.

Turning back to the Turkish ores and slags plotted on Figure 14, it is worth mentioning that the points represent single analyses of a random selection of various minerals. But even at this stage they show certain separation of different deposits (Figure 16). It is nearly certain that many accurate analyses of the samples from these areas would produce a picture very similar to that on Figure 15.



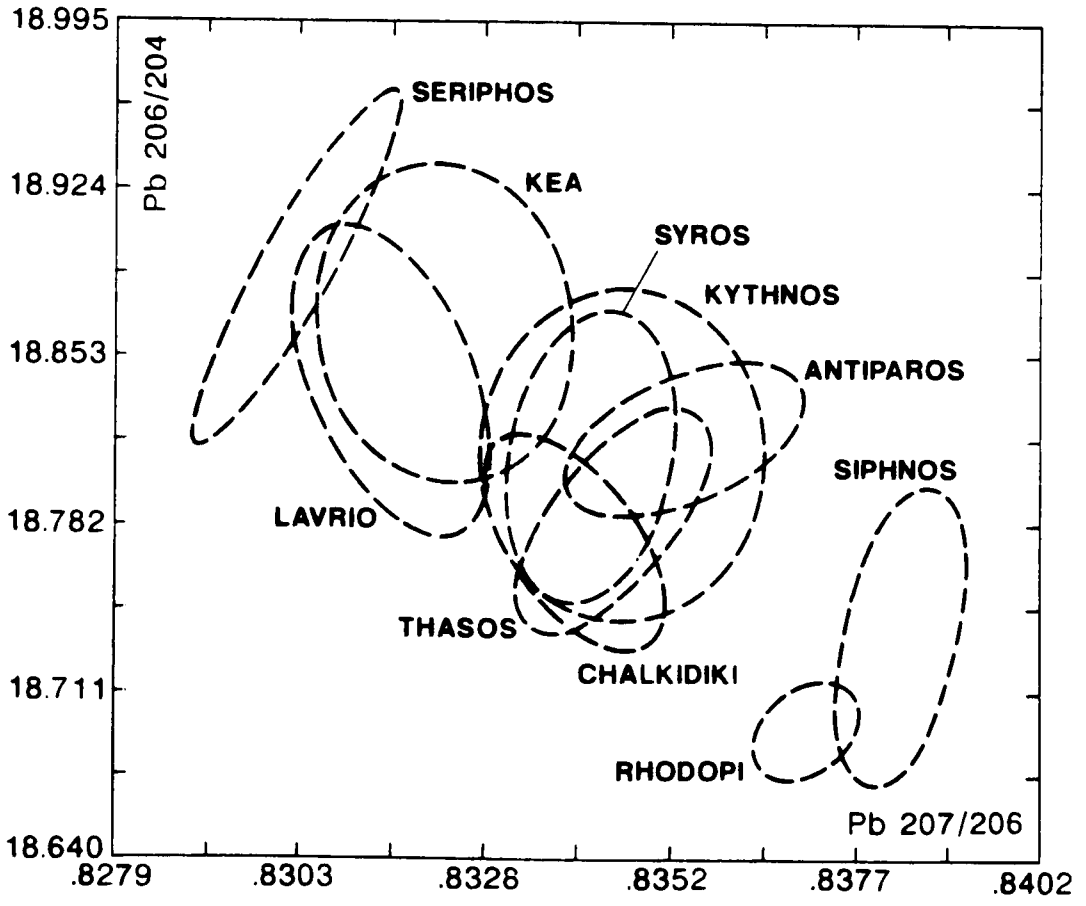


Fig. 15. Lead isotope 'fingerprints' of lead/silver and copper deposits from the Aegean which were used to construct the Aegean Field on Fig. 14. The ellipses were calculated with 95% confidence limits around 10 to 25 data points measured for ore samples (over 100 points for Lavrio and 35 for Kea).

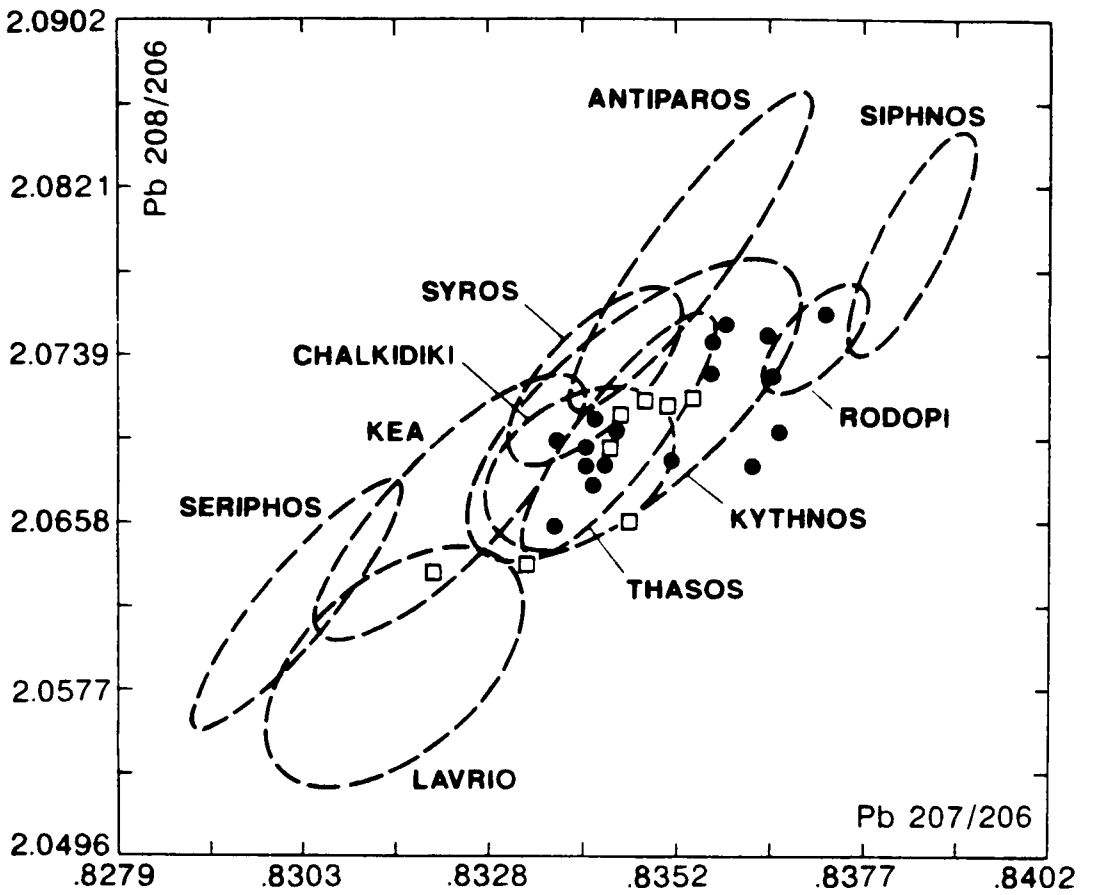


Fig. 16. The Turkish lead and copper ores from Fig. 14 plotted together with of the Greek ore fields. The lead (marked by black circles) and copper (open squares) represent mostly single samples from a large area covering all North-West Turkey. Only many more lead isotope analyses of samples from these deposits will prove, or disprove, their similarity to the Greek ores.

The key point of provenancing using lead isotopic analyses lies in the possibility of discriminating between ore sources if one is to be able to trace a metal artefact to its ore source. Diagrams like that reproduced in Figure 14 represent a most disadvantageous use of lead isotope data. The two most important shortcomings of such an interpretation are the lack of discrimination of the geological character of each of the deposits (some might consist of only lead or only copper/iron ores) and the two-dimensional presentation of the data. It is very important that the deposits which are used for comparison of their lead isotope compositions with the artefacts should contain metals of which the artefacts are made (the original of Figure 14, though based overwhelmingly on the isotopic analyses of lead ores, was used for identification of sources of copper-based metals). Also, it can be misleading to compare artefacts with samples of minerals from small veins of silver-poor galena which have never been exploited. For example, it has been concluded that lead was not exploited in the Bronze Age Aegean except where it contained silver above a certain lower limit (Gale and Stos-Gale 1981, Gale, Stos- Gale and Davis 1984, Pernicka 1989) and fieldwork in this region confirmed the lack of any traces of ancient mining on many of the Aegean islands. The diagram reproduced in Figure 14 does not distinguish between the ore deposits which have silver above or below that limit. It is also very unfortunate that the samples coming from the individual ore deposits are not distinguished, so that a possible group structure is ignored. Additionally, it displays only two out of the three Pb isotope ratios, so that possible extra discrimination available by using all the data is missed.

Begemann et al. (1989) argue that only rarely does the third ratio help to separate the isotope fields; this conclusion definitely is not confirmed by the experience of comparing large numbers of lead isotope data of minerals and artefacts. This statement is most likely rooted again in the geochronologically-related bias, and is based on far too small a number of lead isotope analyses of

minerals from one deposit. The Mainz-Heidelberg group have never published more than six lead isotope analyses on samples of ore from one deposit; indeed the characterisation of the deposits in their publications is mostly based on one or two analyses, or sometimes just a lead isotope composition of a sample of slag from a near-by, undated, slag heap. This approach might sometimes be necessary, because there is still not enough lead isotope data available for ores, but it can be treated **only** as a preliminary assessment of the data and if possible (and there must be in Heidelberg an enormous collection of unanalysed ores from Turkey, for example), many more analyses should be carried out to complete the research. Therefore, the lead isotope analysis of as many mineral samples as possible, from relevant ore deposits is a necessary requirement for any archaeological metal provenance project. On the other hand, the work is not so arduous as it seems: the number of ore deposits is limited, and the same sets of reference data can be used in many different projects.

6.2. Lead isotope characterisation of ore deposits.

Clearly, to make the most of the properties of lead isotope 'signatures' measured for ancient artefacts, it is necessary to accumulate a comparative database of the lead isotope compositions of ore deposits relevant to archaeometallurgy. The work at Oxford for the past decade has concentrated on the metal sources which might have been used in the Bronze Age Mediterranean to supply the needs for the metals lead, silver and copper. This has necessarily meant that the lead isotope compositions have had to be determined for the many copper, and lead-silver, deposits in this region. In assigning the provenance of, say, a copper object to a copper ore deposit on the basis of a match between their lead isotope compositions, it is vital to discover what is the range of lead isotope compositions in a given deposit and whether the lead isotopic compositions of different mineral ore deposits can be distinguished from one another. One important factor which is decisive for this is the accuracy with which lead isotope

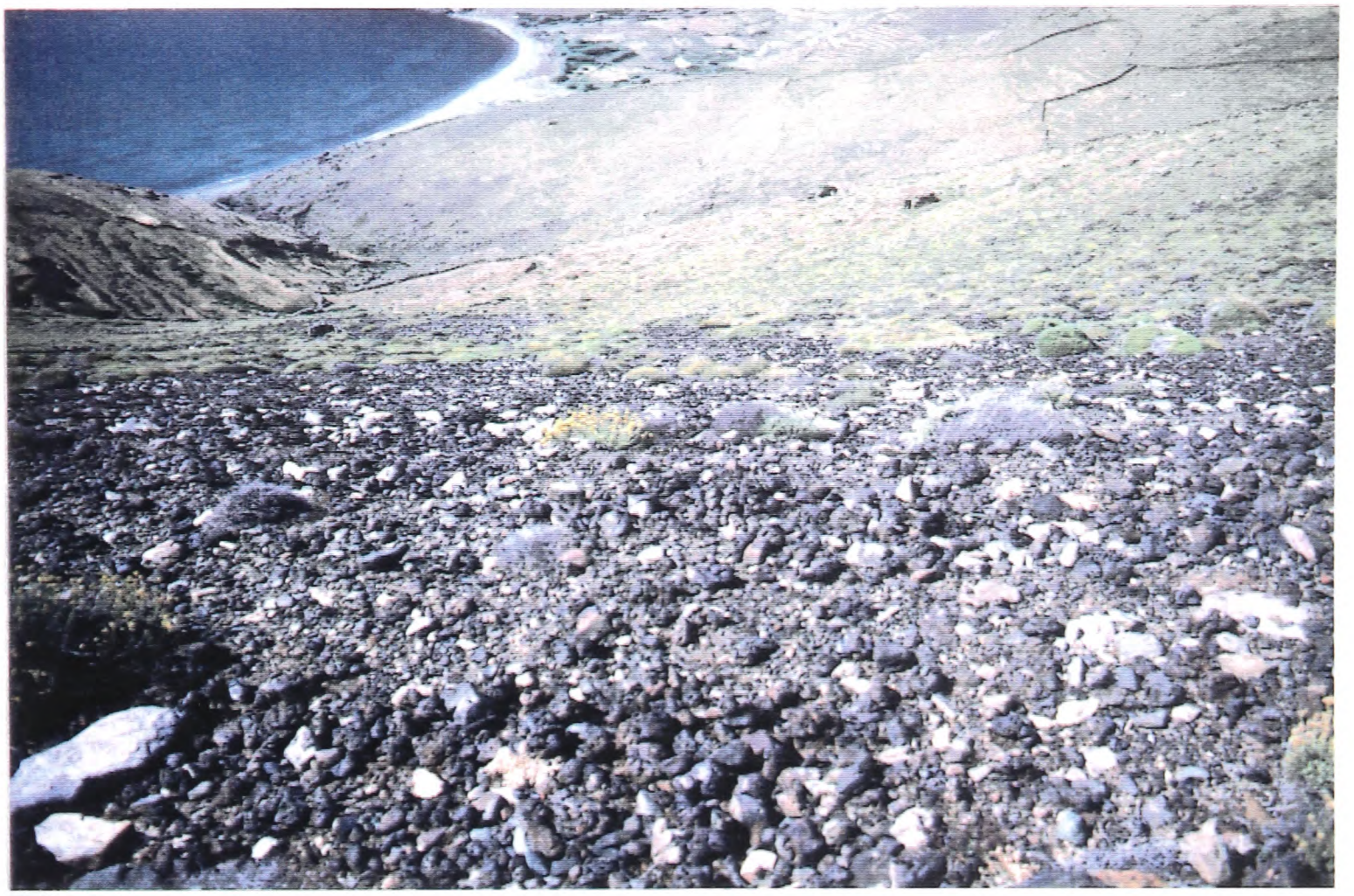
ratios can be determined; another - which I will discuss in this chapter - is the number of samples analysed.

Fieldwork is also necessary to look for any traces of associated mining activities and to explore mines and slag heaps for ceramics or charcoal to date the activities. One will be immeasurably more confident about lead isotope evidence that a Third Millennium copper alloy dagger from Crete was made from copper from the Cycladic island of Kythnos against the background of the dating to that period of the copper slag heap on that island, by ceramic and accelerator C-14 dating (Stos-Gale 1989). At present we have well over a thousand lead isotope measurements of ores from the Mediterranean deposits, for which we have also geochemical information (the mineralogical type of the deposit) and have conducted surveys for ancient mining and smelting activities.

The vital importance of fieldwork in providing a proper basis for lead isotope studies in metal provenancing was recognised also by the German team (Wagner, Pernicka, Begemann et al.) and resulted in several good publications. Their work in Turkey produced the only extensive and well documented archaeometallurgical evidence for the extensive metal deposits on the Anatolian Plateau. Unfortunately, the lead isotope analyses are treated very marginally in their publications. Some archaeometallurgical work, with more emphasis on archaeology than geology, is also carried out there by the Turkish/American team led by Aslihan Yener. However, the number of published lead isotope analyses of ores from the deposits surveyed by them is still very small and includes some data rather unsatisfactory from the geological/archaeometallurgical point of view; for example lead isotope analyses of soil and stream sediments. Altogether there are still only about 150 lead isotope analyses of lead and copper minerals from more than 200 deposits surveyed in Turkey.

Fieldwork involving the search for ancient remains of mining and smelting forms an essential background for the geochemical characterisation of a mineral

Phot. 4. Ancient copper slag heaps on Cycladic Islands in the Aegean provide important material for archaeometallurgical studies. The upper photograph shows an undated slag heap at Kephala on Seriphos; the lower, the Bronze Age copper smelting site on Kythnos.



deposit. However, this should be accompanied by a collection of samples for chemical and lead isotope analyses (as comprehensive as possible, sampling a particular deposit both in depth and areal extent). It seems clear from the analysis of lead isotope data available at present that different deposits might have lead isotope signatures of slightly different range. For example, some ore deposits were reported to have, for samples collected from various positions within the deposit, lead isotopic compositions which are constant within the experimental uncertainty of $\pm 0.1\%$ such as Balya in Turkey (Begemann et al. 1989) and Bleiberg in Austria (Köppel and Köstelka 1976). These are the exception rather than the rule, and it is always necessary to make a number of different analyses for different samples through the deposit in order to establish its isotopic field.

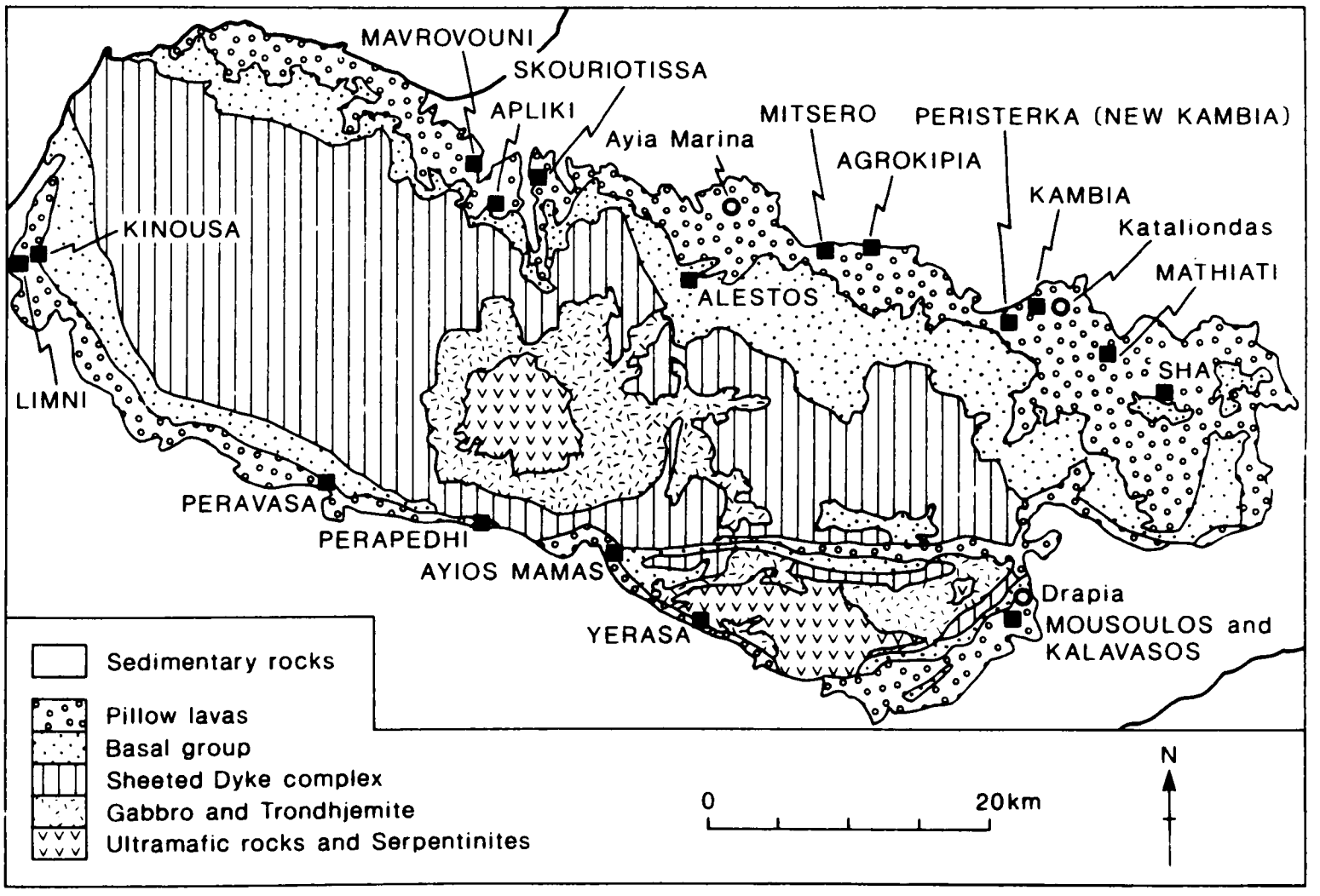


Fig. 17. Copper ore deposits around the Troodos Mountains on Cyprus.

It seems that large mining areas, for example the Troodos mountains region on Cyprus, might superficially look isotopically homogeneous if there

are not enough analyses of ores from each of the single occurrences (or mines). The isotope 'field' for copper ores in the foothills of the Troodos Mountains in Cyprus (Figure 17) was published a few years ago (Stos-Gale et al. 1986) and at the time it seemed that it could be regarded as a uniform range of lead isotope compositions (Figure 18). Recently, we have analysed more samples from Cyprus and it became apparent that with more analyses of samples from the same area of mineralisation (or from the same mine) the superficially uniform group breakes down into sub-groups. The increased number of data points shows that it is possible to distinguish the distinct isotope ranges for ores from specific occurrences on this island. Figure 19 is an updated computer-derived diagram which shows a clear distinction between the eastern mines of Mathiati and Kambia, Pitharokoma and Peristerka (called also New Kambia) and the mines of Limni and Alestos. Copper carbonates from Troulli also stand out separately; this deposit is of quite different geological character and is situated north of Larnaca, in the eastern part of Cyprus, well outside the Troodos massif. This result is quite contrary to the statement of Knapp (1991) that lead isotope fields expand when more data is available. In this case the fingerprints of specific deposits contract visibly.

The diagram of Figure 19 has been drawn using two lead isotope ratios, each referred to ^{204}Pb, because this gives the best visual demonstration of the divisions using only two dimensions; incidently, this is the usual representation of lead isotope data in geological publications. The four lead isotope abundances make only three independent lead iostope ratios, but naturally, it is quite simple to recalculate them into any other set, which might sometimes be beneficial for graphical illustration.

It seems possible that the Cypriot lead isotope signature, as presented and used until now, consists in fact of several separate signatures characteristic of geographically different deposits. This was suggested already by Hamelin et

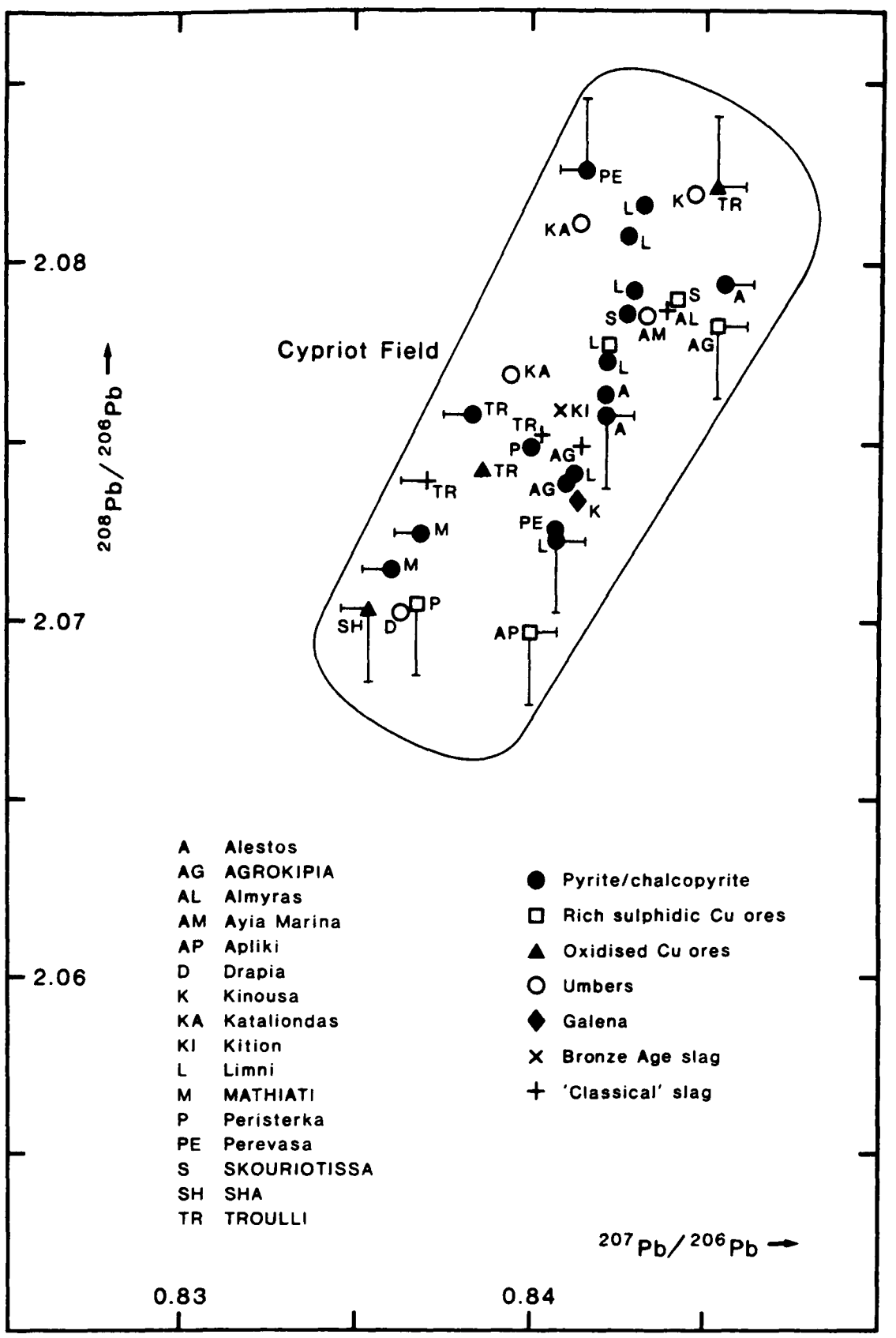


Fig. 18. Cypriot lead isotope field based on a few lead isotope measurements of ores from different mines.

al. (1988) but the insufficient number of analyses available at the time made their suggestion unconvincing.

A similar situation is represented by the analyses of ores from various deposits in the Othrys Mountains in central Greece (Figure 20). We made two brief surveys of these mountains in 1988 and 1990. The copper deposits there are

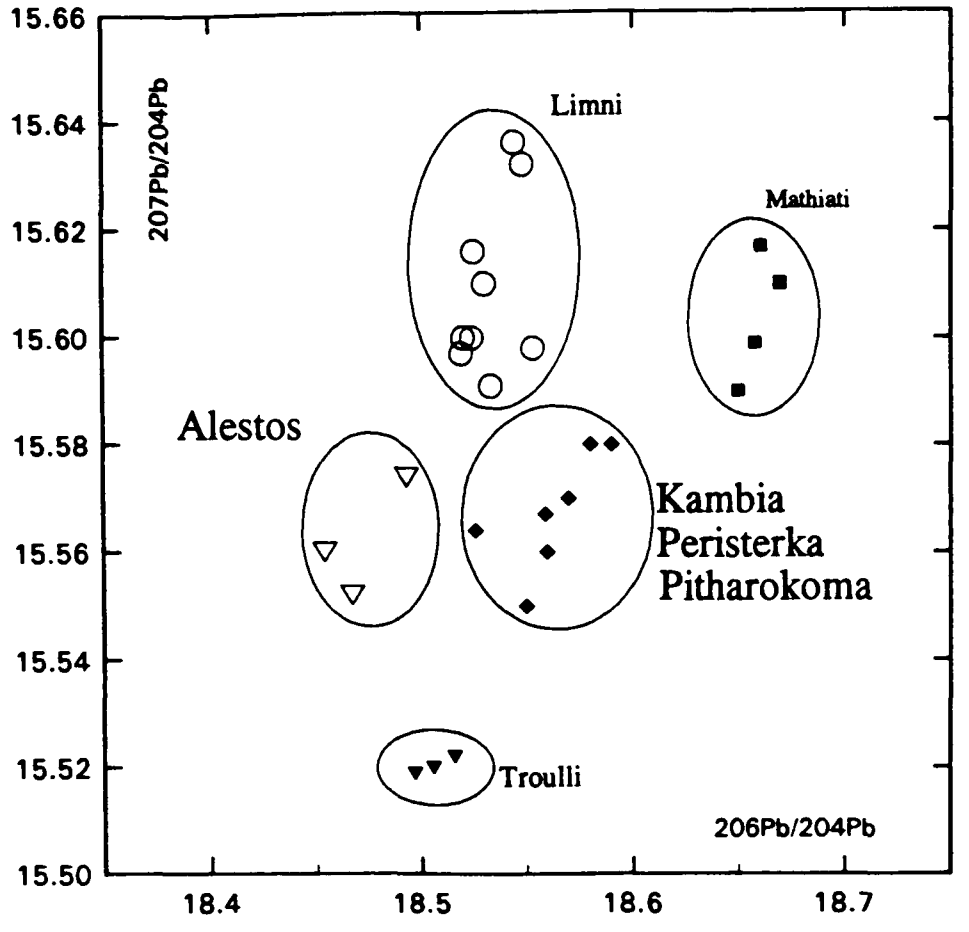


Fig. 19. Increased number of lead isotope analyses of minerals from the same mine shows that within the large 'Cypriot field' there are regions characteristic for specific mines and mining areas.

associated mostly with volcanic rocks and are scattered around a large area. In several locations, not necessarily in the same locations as the ores, are scatters or large heaps of copper slag. Some of them we had dated in the C-14 Accelerator Laboratory at Oxford and they proved to be from the geometric, Archaic and Classical periods (8th to 5th century BC). So far, we have analysed only 15 ore and slag samples from these occurrences, but it seems possible that more analyses will show again a sub-structure of groups, differentiating between the mines and slags of Limogardion, the limonitic mines of Stagira and outcrops of copper carbonates in Krio Vrisi. The two samples from Ano Agoriani and one from Krio Vrisi plot rather too far apart and repeated measurements of these ores are clearly necessary (Figure 20).

Another area which shows a large range of close lead isotope compositions is that of the lead/zinc/copper deposits in Tuscany (Italy). Figure 21 shows the small groups formed by Tuscan ore deposits. It is worth emphasising, however,

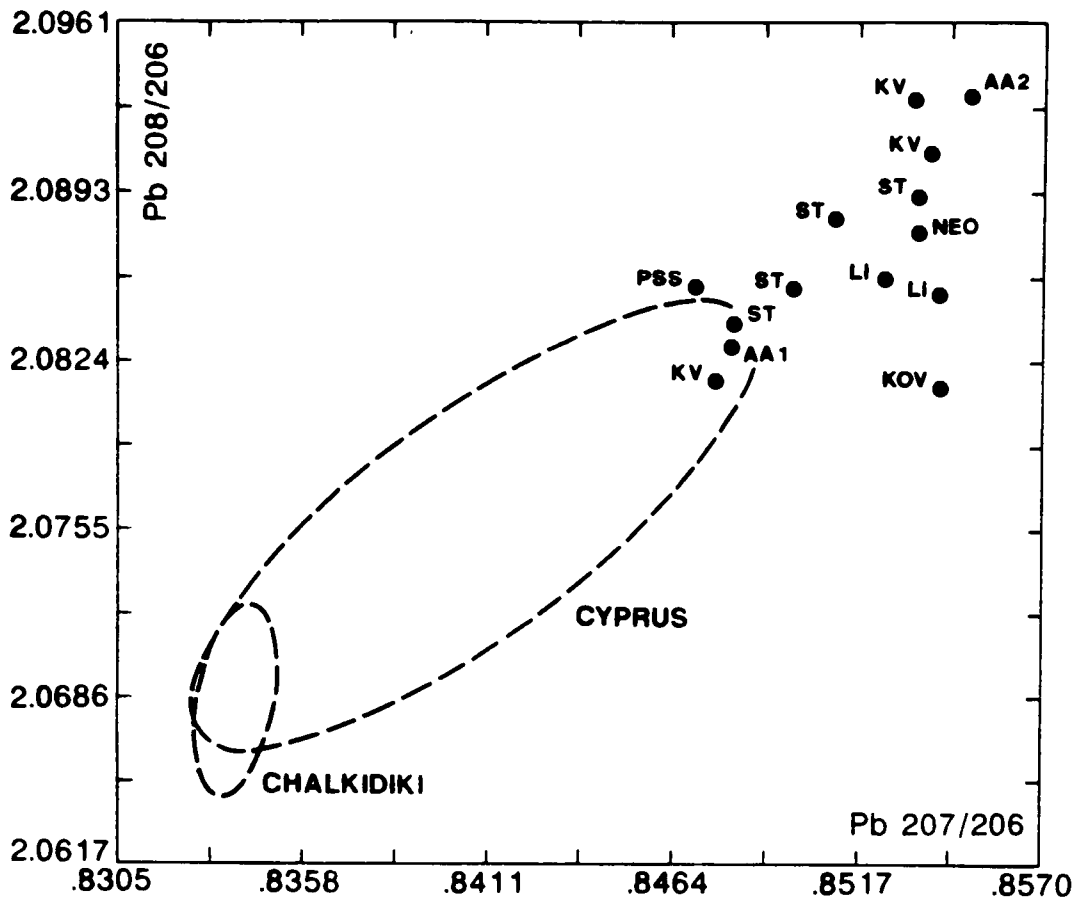


Fig. 20. Lead isotope analyses of ores from occurrences in the Othrys Mountains in central Greece. LI - Limogardion, KV - Krio Vrisi, KOV - Koukuli Vracho, NEO - Neochorio, ST - Stagira, AA - Ano Agoriani, PSS- Palea Sparta.

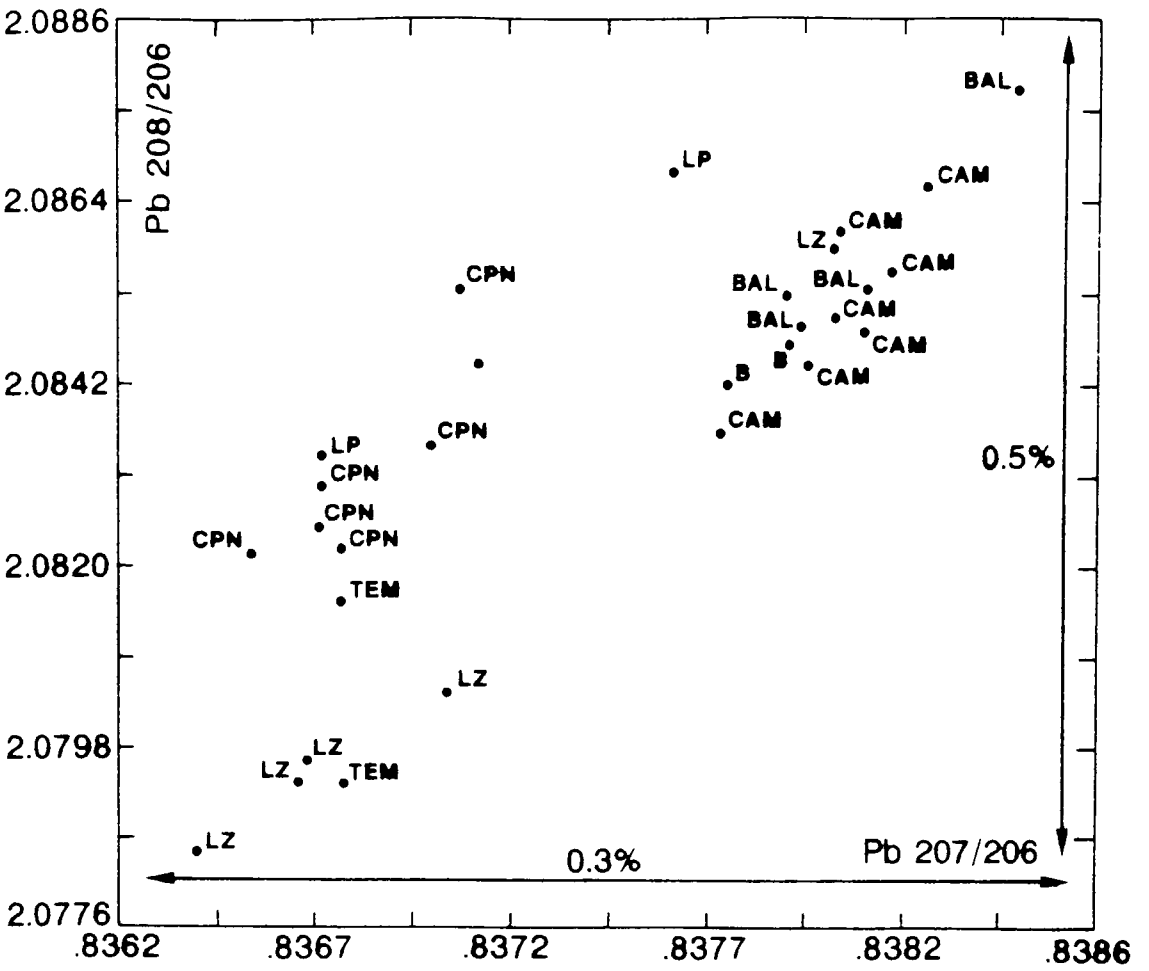


Fig. 21. Lead isotope analyses of ores from Tuscany. Minerals from different mines group in separate parts of the diagram. BAL - Balerino, LZ - Lanzia, CAM - Campiano, CPN - La Capenina, TEM - Temperino, LP - La Pesta, B - Baciolo. All these samples were analysed with accuracy better than 0.05% and cluster very closely together. The range of their lead isotope ratios is shown on the diagrams.

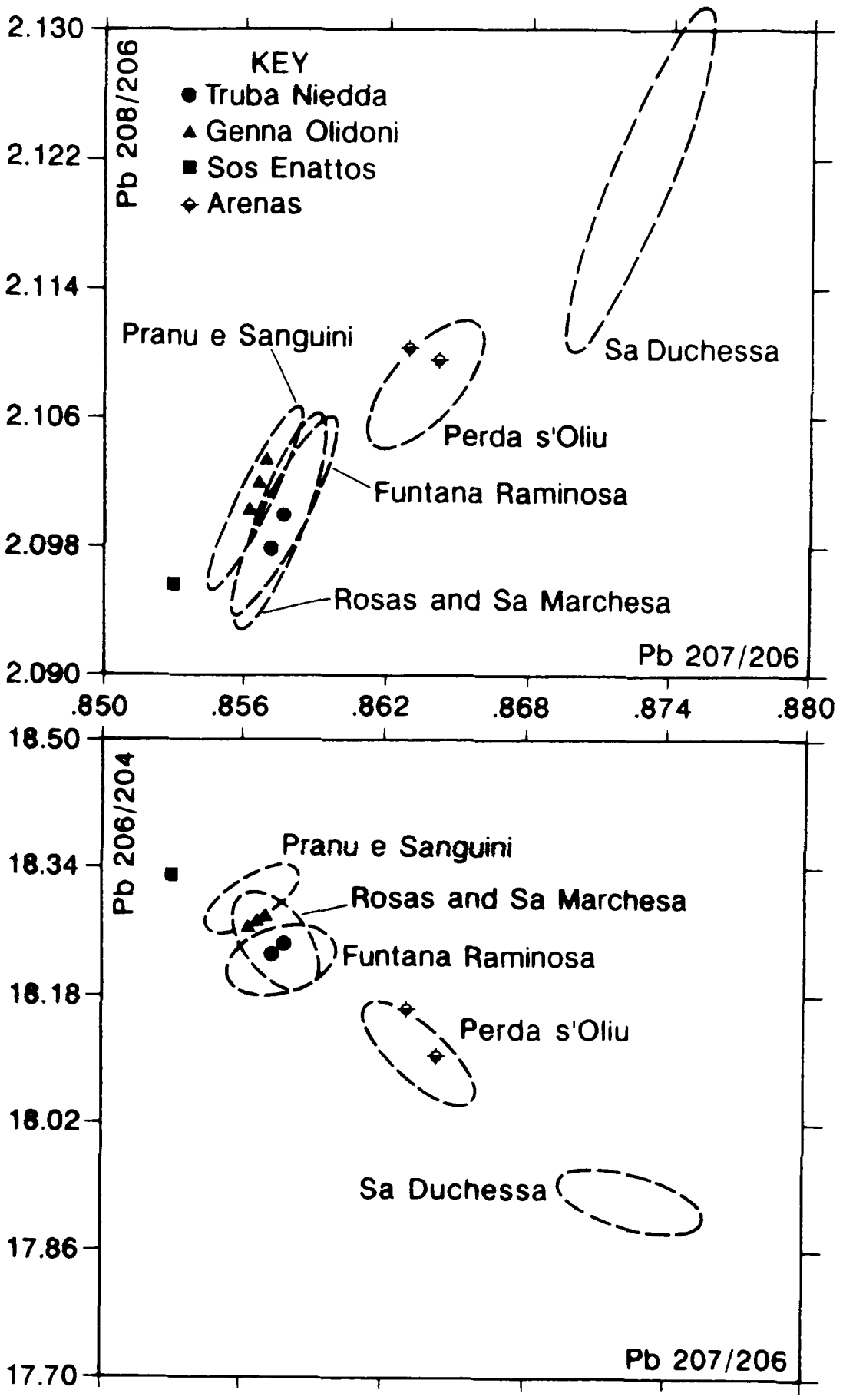


Fig. 22. Lead isotope compositions of different mining regions of Sardinia. The geological history of this island is much more complex than that, for example, of Cyprus. This is reflected in strongly varied lead isotope compositions of different geological formations - the ellipses were calculated with a 95% confidence level around at least five data points.

that all these three large mining areas (Cyprus, Othrys and Tuscany) have lead isotope characteristics which cluster very closely together and in a way it is still possible to decide that the origin of an ancient metal object is consistent with 'Cyprus' or 'Tuscany', because the range of lead isotope compositions for all groups of different mines is rather small, and also it is not impossible that in antiquity several mines in the same area were exploited and the artefacts were made from ores not necessarily coming from just one mine. Again, this suggestion could be only sometimes true - we have noticed already that for example the Cypriot Late Bronze Age oxhide ingots plot only in one part of the large 'Cypriot' field, which might indicate that only a few of the mines were in fact producing copper for those huge ingots (Gale 1991).

Quite a different geochemical picture is presented by the complicated multimetallic deposits on Sardinia. There, the range of lead isotope compositions is very large (more than 2%) and different deposits have distinctly different and separate lead isotope ratios (Figure 22). This reflects the geological ages of these ore deposits, which range from Cambrian to Tertiary. Additionally, many of the mines are chiefly lead/zinc deposits and only some have copper minerals. A 'Sardinian' field constructed from all the data put together would cover a vast area and has no value for the identification of the origin of ancient metals. Archaeological objects made of copper based alloys should not be compared with lead/zinc deposits and *vice versa*. Again, the large number of analyses of ore samples from the same mine demonstrates that there is no basis for Begemann's gloomy conclusion (1989, 275) that the overlap between Sardinian ore deposits makes assignment to individual deposits impossible. Table 3 (in Chapter 6.3) shows clearly that there is separation between most of the deposits (Sa Duchessa, Perdu S'Oliu, Pranu e Sanguini and Funtana Raminoza). It seems that Begemann's remark was again a result of a judgment based on an insufficient number of measurements.

The deposits mentioned above show distinct differentiation of lead isotope signatures within one area of mineralisation, showing discrimination between occurrences sometimes only a few kilometers apart. This conclusion is not unexpected. First, a geographical area may contain ore deposits of quite different geological age (as on Sardinia). Then, as was mentioned in previous chapters, remobilisation, the insufficient mixing of lead prior to mineralisation, or a small inclusion of lead from the surrounding rocks might change the isotope composition. It seems, however, that a significant differentiation between several occurrences in one large area of mineralisation is not necessarily the rule. One of our best characterised copper/lead/silver deposits, that of Lavrion in Attica (well over 100 measurements), so far does not show any visible sub-structure within the analyses of presently collected ores. However, when analyses of ancient, locally excavated, litharge and lead from silver smelting sites of Agrileza (Ellis Jones 1985) and Thorikos are taken into account, then the 'field' extends slightly, and this might indicate that in fact the lead/silver minerals exploited in Antiquity were mined from parts of the deposit which are slightly different from the main ore body. We were not yet able to find ores with such an isotope composition during the geological fieldwork in Lavrion, but no ores near Agrileza have been sampled. Figure 23 shows our lead isotope data for modern ores and for the 5th century BC lead and litharge from the archaeological excavation of ancient silver smelting sites in Agrileza and Thorikos.

Quite another problem is presented by our analyses of copper slags and ores from the island of Kythnos in the Cyclades. The mineral deposits of Kythnos are quite small in comparison to the big mining areas mentioned previously. Modern (1941) mining on Kythnos was for iron and only some small percentage of copper in the iron ores indicates that the mineralisation is of a mixed type. Possibly more copper minerals, and particularly copper-rich malachite and azurite, might have existed in the oxidation zone on the surface of the deposit, which

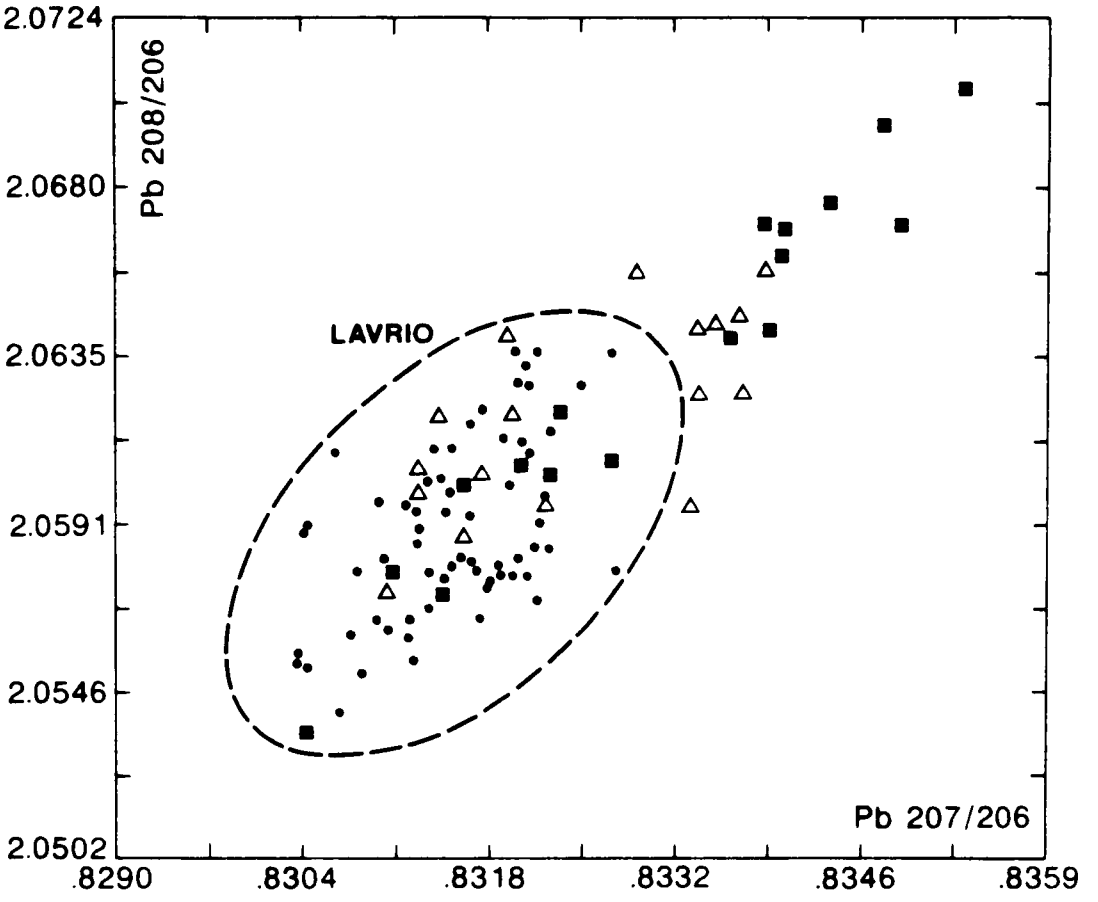
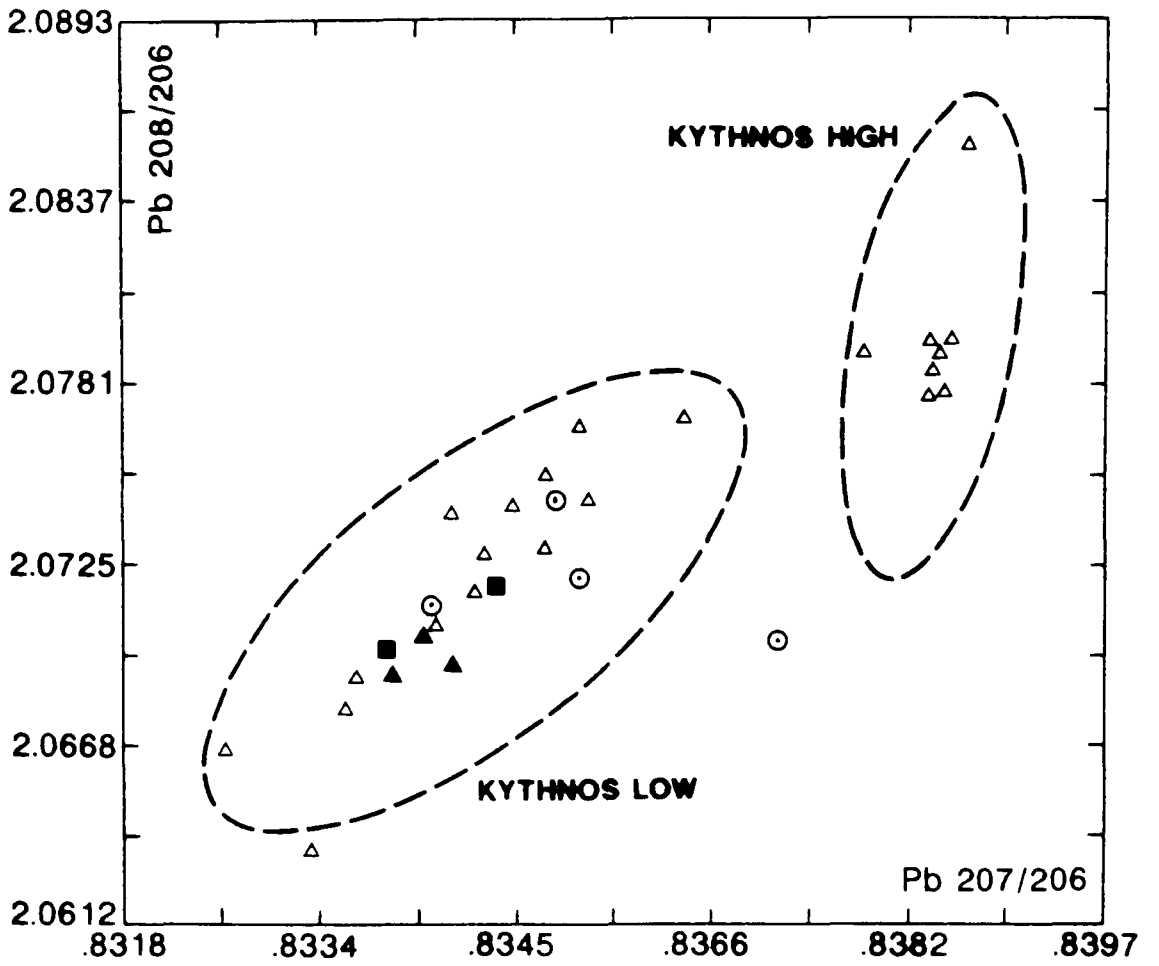


Fig. 23. Lead isotope data from the modern lead and copper minerals from the Greek deposit of Lavrion compared with lead isotope compositions of the ancient (5th century BC) products of silver extraction from the archaeological excavations in the same locality.



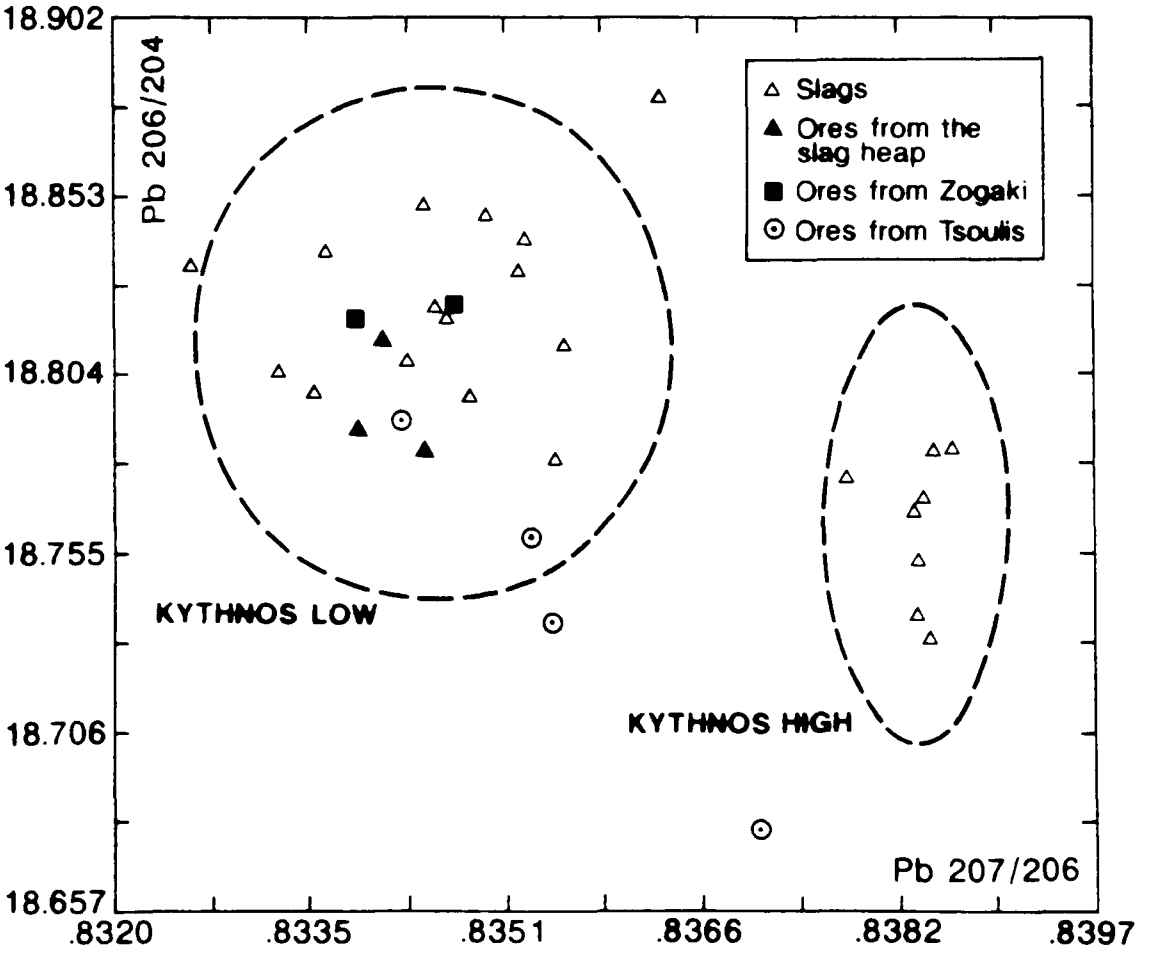


Fig. 24. The lead isotope analyses of slags and ores from the Cycladic island of Kythnos. The ores from the island plot only in the lower part of the Pb 208/206 diagram.

has been obliterated by the iron mining. On the other hand, on this island we have found and dated the earliest copper smelting site in Europe (2800 BC, see Stos-Gale 1989) where pieces of rich copper ores were found mixed with the slag. For the purpose of establishing which of the Bronze Age copper objects were made of copper smelted on this island, the lead isotope 'field' for Kythnos has been constructed largely by measuring the lead isotope composition of ores and slags collected on the slag heap (Stos-Gale 1989) and only a few copper ores from the mines. Careful examination of the structure of the plotted data (Figure 24) shows that ore samples from Tsoulis, Zogaki and from the slag heap cover a rather small range in the lower part of the diagram, whilst in the upper part of the diagram several samples of copper slags form a separate group. The whole Kythnian field covers again a rather large range of isotope compositions (nearly 1%) and since the samples are of slags, not of ores, it is very difficult to be sure that all of them indeed are characteristic of Kythnian minerals. In the second, archaeological, part of my dissertation I will discuss again in detail the possible composition and origin of this slag. It seems, however, that in this particular case it might be worth leaving the description of the copper metal of this particular origin as 'Kythnos' (perhaps dividing it into 'low' and 'high'), meaning the origin of metal **smelted** there, rather than the copper ore occurring on Kythnos. On the other hand this set of data cannot be used for any assessments of the lead isotope characteristics of copper minerals from this island, until more lead isotope analyses are made for ores collected in situ on Kythnos.

6.3. Separation of lead isotope fields for different ore deposits.

Discrimination between two ore deposits having similar lead isotope compositions is vital to metal provenancing; it depends not only on the precision and accuracy of the isotopic analyses, but also on the proper experimental definition of the range of isotopic compositions found in each ore deposit.

Table 3 shows a list of lead isotope data for all lead/silver/copper deposits which might be relevant to archaeometallurgical provenance studies for European and Near Eastern artefacts, and for which I could find five or more lead isotope measurements. We have many more lead isotope data for samples from ore deposits in different parts of Europe, Egypt, Iran and India, but they are only preliminary data consisting of fewer than five measurements. These results can be used only as indicators of the general lead isotope compositions of those deposits and have no statistical value. They can be used for comparison to ancient artefacts only for a preliminary assessment of their origin, because such a small sample of ores might not be sufficiently representative of the three-dimensional lead isotope 'fingerprint'. On the other hand, a high proportion of such preliminary measurements is so different from any other 'fingerprints' of well-characterised deposits that just on the basis of one or two analytical points they can be excluded or included as a possible source of an artefact.

It was decided that in order to test as many geographically different deposits as possible in the statistical evaluation of data, all metal ore sources which might have been of importance in Antiquity, and for which at least five lead isotope data can be found, should be included. From the point of view of statistical analysis, a much larger number of measurements should be used, but at least this compromise can provide for the first time numerical values of the range of lead isotope compositions in those deposits and evaluate the possibility of discrimination. On purely experimental grounds, it seems at present that about 20 analyses of different minerals from the same deposit are necessary for its accurate description ('fingerprint'). So far, however, there seem to be remarkably few deposits for which 20 published analyses exist. However, at least some preliminary assessment of all these data seems worth while at present.

The results compiled in Tables 3 and 4 are largely from the database of the Isotrace Laboratory and were measured by my colleagues and me. They

are indicated in the table by the letter O (the Mediterranean ore samples were collected by myself, Dr. Gale and members of the local geological service, minerals from Wales come from the collection of Brenda Rohl). Other data were taken from recent publications of the laboratories in Max- Planck Institute für Chemie, Mainz (M), NIST/Smithsonian (S) and from the geochronological data base of Dr. Bielicki in Leipzig (L). Figures 12 a and b show the geographical locations for most of the deposits listed in these two tables.

The statistical parameters of the data in Tables 3 and 4 were calculated using the commercial BMDP statistical software (program 2d). This program calculates the mean, median and standard deviation, skewness and kurtosis and extreme values. A histogram and a line plot are displayed and Shapiro and Wilk's W statistic is applied for testing normality of the data distribution. The W statistics calculated for these data are in a great majority of cases consistent with a normal distribution ($0.9 < W < 1$) (Shapiro and Wilk 1965). This result is very encouraging because many statistical methods rely on the normality of the distribution of data points. However, at present this conclusion must be treated cautiously, because in most cases the number of data is rather small and the normal distribution was checked only for pairs of lead isotope ratios. This does not constitute a full test of normality for the trivariate lead isotope distribution.

Table 3 lists the ore deposits in order of their mean lead isotope composition and gives the standard deviations calculated by BMDP 2d. This comparison demonstrates clearly that the mean lead isotope values for the three independent lead isotope ratios for all those deposits cover a wide range of values (8%, 16% and 17% respectively).

The standard deviations of the lead isotope ratios for ore deposits are listed in the table; these are a measure of the geological spread in isotopic composition superimposed on the analytical accuracy of the measurements. The an-

alytical accuracy of all lead isotope measurements included in this table should be equal to or better than 0.1%; it is however not possible to be sure of such accuracy for absolutely *all* measurements gathered here. On theoretical grounds one could argue that the standard deviation of lead isotope data from a geochronologically uniform deposit will depend not only on the accuracy of the isotope measurements, but also on the natural isotope inhomogeneity within the deposit. So far, there is no proof that in each of the individual deposits there is no such inhomogeneity and therefore the selection of samples for isotope analyses might significantly influence the resulting 'fingerprint'; for example, if there is a slight difference in lead isotope composition either with depth or in a horizontal sense, then this will not be evident in the lead isotope measurements if the samples for analyses are collected from the same homogeneous vein or outcrop. On the other hand, even a smaller number of minerals collected from different veins or outcrops can produce a significantly larger isotopic range and therefore larger standard deviation within a group. For example, four samples of galena from the region of Kallianou on the island of Euboea in the Aegean come each from a different galleries in the same area of mineralisation. The standard deviations of respective lead isotope ratios of those 4 samples is .0021, .00056 and .00605 respectively. In comparison with that, 81 samples of galena and copper ore from different outcrops in Lavrion show standard deviations of .00212, .00054 and .0269. The quality of the measurements in both groups is the same (0.1%); the samples were analysed on our old single collector mass spectrometer. The new sets of data on ores from the new multicollector machine have much better accuracy of measurements within a single run (typically overall standard error for a run is around 0.002 for the 206 ratios and .007 for the ratio with respect to the isotope 204. It is interesting to notice though that a number of groups of recent very good measurements from our laboratory still show standard deviations within a group of samples of the same order as the

old data. For example, standard deviations calculated for recent measurements of galenas from Olkusz are respectively .00155, .0028 and .0248; and for Essimi .00108, .00299 and .0087, whilst old measurements for Chalkidiki show standard deviations of .00159, .00049 and .0182; and for Seriphos .00190, .00041 and .0283 (Table 3).

A more careful examination of Table 3 demonstrates that there are no two deposits with all three mean ratios identical. Bearing in mind that all three ratios have to be taken into account, examination of the data at even this simple level demonstrates that many of these ore deposits can readily be distinguished.

On the other hand, there are many important deposits which are characterised by lead isotope ratios which have mean values lying closer than even 1σ distance. The best approach to separate such ore deposits lies in statistical discriminant analysis; in practice the use of linear discriminant analysis seems to be quite satisfactory. One approach to discrimination is in defining Mahalanobis distances (Mahalanobis 1948). This method takes into account correlations between variables and therefore is suitable for lead isotope ratios which are correlated to a considerable degree. The program used for the statistical evaluation of the lead isotope data will be discussed in further chapters, but already it can be seen that, apart from the mean value, the other crucial aspect of lead isotope fingerprinting of ore deposits, is the 'size' of each fingerprint which will be represented by the range of the measured lead isotope ratios.

Table 4 lists the same deposits as Table 3 but in a different order and shows the percent range of lead isotope ratios (calculated from the difference of the two extreme values) within one group of ores and the measure of normality of the distribution represented by the Wilk's W. Listing in the order of the number of samples from each deposit which were analysed underlines the correlation (or lack of it) of the per cent range of isotope ratios covered by one ore deposit to the number of samples analysed. A glance at Table 4 confirms the important

Table 3. Mean lead isotope ratios of ores from different ore deposits. Data annotated with 'O' was measured at Oxford. Other groups of data were taken from publications of three groups: Heidelberg-Mainz (M), the Smithsonian (S) and Dr. Bielicki in Leipzig (L).

Deposit	Country	Ores analysed	Mean 208/206	SD 8/6	Mean 207/206	SD 7/6	Mean 206/204	SD 6/4
Keban (M)	Turkey	5	2.04418	.00077	.81986	.00068	19.150	.0111
Thera (O)	Greece	12	2.05816	.00230	.82747	.00055	18.968	.0170
Lavrion (O)	Greece	81	2.05898	.00212	.83157	.00054	18.842	.0269
Ergani (M+O)	Turkey	11	2.06072	.00422	.82892	.00416	18.880	.1050
Seriphos (O)	Greece	12	2.06180	.00190	.83027	.00041	18.885	.0283
Taurus2b (S)	Turkey	7	2.06209	.00166	.83125	.00131	18.942	.0304
Troad S-2 (M)	Turkey	9	2.06590	.00133	.83389	.00048	18.755	.0199
Kea (O)	Greece	30	2.06721	.00206	.83194	.00039	18.879	.0169
Chalkidiki (O)	Greece	16	2.06857	.00159	.83396	.00049	18.774	.0182
Essimi (O)	Greece	19	2.06907	.00108	.83581	.00299	18.727	.0087
Balya (O+M)	Turkey	9	2.07002	.00130	.83431	.00038	18.804	.0130
Thasos (O)	Greece	18	2.07033	.00237	.83448	.00052	18.783	.0194
Balya (M)	Turkey	5	2.07096	.00099	.83423	.00020	18.810	.0070
Wiesloch (O)	Germany	6	2.07166	.00134	.83632	.00016	18.698	.0216
Taurus 1b (S)	Turkey	8	2.07299	.00113	.83481	.00083	18.782	.0188
Syros (O)	Greece	25	2.07309	.00150	.83420	.00041	18.811	.0227
Cabo da Gata(O)	Spain	17	2.07322	.00122	.83543	.00083	18.768	.0270
Kythnos (O)	Greece	29	2.07404	.00442	.83543	.00178	18.796	.0339
Troad S-1 (M)	Turkey	13	2.07406	.00127	.83567	.00040	18.755	.0013
Kirki (O)	Greece	11	2.07491	.00082	.83706	.00021	18.693	.0067
Cyprus (O)	Cyprus	39	2.07576	.00354	.84074	.00308	18.532	.0749
Antiparos (O)	Greece	15	2.07887	.00251	.83546	.00098	18.822	.0464
Siphnos (O)	Greece	23	2.07940	.00200	.83831	.00035	18.832	.0250
Mazzaron (O)	Spain	7	2.07984	.00120	.83645	.00040	18.725	.0064
Euboea (O)	Greece	4	2.07997	.00210	.83982	.00056	18.664	.0061
Taurus 2a (S)	Turkey	11	2.08055	.00342	.84089	.00086	18.704	.0371
Ai Bunar (O)	Bulgaria	12	2.08214	.00250	.84431	.00078	18.494	.0219
Tuscany (O)	Italy	31	2.08382	.00237	.83748	.00065	18.753	.0257
Othrys(O)	Greece	16	2.08672	.00380	.85172	.00260	18.354	.1010
Olkusz (O)	Poland	12	2.08763	.00155	.84842	.00280	18.455	.0248
Rammelsberg (L)	Germany	15	2.09090	.00200	.85565	.00046	18.232	.0230
Sa Marchesa (O)	Sardinia	5	2.09807	.00200	.85716	.00084	18.253	.0344
Halsbrucke (L)	Germany	14	2.09910	.00216	.85163	.00182	18.336	.0467
Funtana (O)	Sardinia	11	2.09972	.00329	.85780	.00190	18.220	.0470
Pranu (O)	Sardinia	6	2.10102	.00240	.85650	.00080	18.302	.0174
Wales (O)	UK	8	2.10432	.00132	.86121	.00030	18.171	.0260
Fenugu (O)	Sardinia	15	2.10503	.00310	.86051	.00207	18.207	.0474
Montevecchio(O)	Italy	11	2.10732	.00217	.86163	.00180	18.155	.0499
Perda s'Oliu(O)	Sardinia	6	2.10813	.00160	.86360	.00100	18.108	.0272
S. Giovanni (O)	Sardinia	9	2.11819	.00550	.87166	.00350	17.939	.0870
Dariba (O)	India	10	2.22461	.01347	.96483	.00358	16.090	.1000

Table 4. Range of lead isotope ratios in ore deposits (calculated from the diffrence between the two extreme values.

Deposit	Country	Ores analysed	% range 8/6	Wstat 8/6	% range 7/6	Wstat 7/6	% range 6/4	Wstat 6/4
Euboea (O)	Greece	4	.23	.98	.15	.85	.07	.75
Keban (M)	Turkey	5	.08	.68	.21	.81	.13	.90
Balya (M)	Turkey	5	.11	.88	.06	.71	.10	.88
Sa Marchesa (O)	Sardinia	5	.26	.96	.24	.97	.38	.83
Perda s'Oliu(O)	Sardinia	6	.18	.90	.30	.85	.43	.88
Wiesloch (O)	Germany	6	.20	.92	.50	.89	.31	.90
Pranu (O)	Sardinia	6	.34	.94	.27	.72	.24	.92
Mazzaron (O)	Spain	7	.19	.89	.13	.93	.10	.91
Taurus2b (S)	Turkey	7	.19	.88	.49	.97	.48	.92
Taurus 1b (S)	Turkey	8	.16	.89	.33	.98	.35	.94
Wales (O)	UK	8	.17	.87	.10	.88	.42	.84
Troad S-2 (M)	Turkey	9	.18	.91	.16	.95	.32	.93
Balya (O+M)	Turkey	9	.21	.99	.14	.93	.20	.94
S. Giovanni (O)	Sardinia	9	.72	.90	1.00	.74	1.25	.80
Dariba (O)	India	10	1.80	.93	1.20	.98	1.60	.90
Kirki (O)	Greece	11	.11	.93	.09	.92	.11	.95
Montevecchio(O)	Italy	11	.30	.82	.58	.86	.68	.86
Funtana (O)	Sardinia	11	.45	.94	.87	.95	1.04	.87
Taurus 2a (S)	Turkey	11	.45	.93	.34	.85	.79	.94
Ergani (M+O)	Turkey	11	.63	.94	1.50	.85	1.56	.86
Olkusz (O)	Poland	12	.23	.92	.10	.95	.43	.95
Ai Bunar (O)	Bulgaria	12	.38	.85	.28	.77	.40	.97
Thera (O)	Greece	12	.39	.96	.22	.91	.28	.95
Seriphos (O)	Greece	12	.48	.97	.16	.93	.59	.96
Troad S-1 (M)	Turkey	13	.21	.96	.19	.96	.21	.92
Halsbrucke (L)	Germany	14	.54	.90	.70	.91	.80	.89
Rammelsberg (L)	Germany	15	.26	.84	.17	.88	.51	.89
Antiparos (O)	Greece	15	.37	.86	.52	.89	1.23	.69
Fenugu (O)	Sardinia	15	.44	.87	.62	.81	.71	.87
Chalkidiki (O)	Greece	16	.25	.96	.22	.96	.31	.93
Othrys(O)	Greece	16	.56	.94	.89	.86	2.00	.96
Cabo da Gata(O)	Spain	17	.22	.94	.44	.65	.43	.91
Thasos (O)	Greece	18	.42	.92	.23	.90	.36	.94
Essimi (O)	Greece	19	.17	.95	.12	.95	.20	.91
Siphnos (O)	Greece	23	.38	.98	.18	.92	.46	.96
Syros (O)	Greece	25	.30	.96	.20	.97	.39	.90
Kythnos (O)	Greece	29	.76	.95	.70	.84	.63	.96
Kea (O)	Greece	30	.36	.93	.16	.95	.31	.91
Tuscany (O)	Italy	31	.44	.93	.28	.91	.63	.98
Cyprus (O)	Cyprus	39	.63	.95	.49	.96	1.80	.96
Lavrion (O)	Greece	81	.46	.97	.24	.96	.72	.97

conclusion that for many ore deposits the range of data for all samples from one mineral occurrence is consistently below, or a little above 0.5%. On present evidence, it seems that there is no significant increase in the lead isotope range of a deposit when the number of samples measured is between 10 and 20 samples (mean value for all three ratios is 0.34%, 15 ore deposits) and when more than 20 samples are measured (0.37%; 5 deposits). The range, however, is considerably smaller for the groups of ores where the number of samples is smaller than 10 (mean of 0.23%; 13 deposits). Larger ranges of lead isotope ratios were found for Dariba, Ergani, Othrys and Cyprus (Kythnos of course must be excluded from this comparison). All of these deposits consist of several different occurrences scattered over a large geographical area and, as has been explained previously, might include smaller groups within the large group. Only a much larger number of isotope analyses of many minerals from each of the single mines in these districts can give us the real range of isotope ratios for each occurrence.

The other two deposits which in Table 4 show a rather large range of lead isotope compositions, Antiparos (Cyclades) and S. Giovanni (Sardinia), include samples collected by geologists and given to us as 'Antiparos' or 'S. Giovanni', but the origin of some of the samples may be doubtful. So far, we have not investigated this matter any further, since we have not yet found any Bronze Age lead or silver objects which match these ores.

It has to be emphasised, however, that each ore occurrence is geologically specific and one cannot assume that the 0.5% range is true for all deposits. If the geological history of an area is complicated, then a very individual approach must be taken into defining the lead isotope 'field' of such a deposit (see for example Hauptmann et al. 1992). Therefore, before any evaluation of a set of 'fingerprints' of ore deposits two points must be strictly observed: *1.* the geology of the deposit must be well known, particularly if there are any signs of remobilisation, high and variable U/Pb ratios in the ores, mineralisations in

geochronologically distinctly different parts of the deposit, etc., and *2.* many analyses of ores from each zone of mineralisation must be run. On the present evidence, it seems that in one mono-geochronological mineralisation the range of lead isotope ratios does not depend *crucially* on the number of samples analysed. For example, 19 samples from Essimi show a range of 0.17%, whilst 4 samples from Euboea are 0.23% apart (these values are for the 208/206 ratios). However, since the correct information about the range of lead isotope compositions in a deposit certainly depends very strongly on the correct selection of samples (from different parts of the mineralisation), a selection of at least 10 different samples will guarantee a better representation than ,say, 5, and 20 will be even more accurate. A general recommendation perhaps should be that more than 20 samples from different parts of the deposit should provide a starting point for its lead isotope characterisation. At present, there are rather few deposits which fulfil this requirement (7 in Tables 3 and 4).

6.4. Presentation and interpretation of the data.

The best initial way of comparing lead isotope data of minerals and artefacts is achieved by plotting the data on lead isotope diagrams. It is possible to construct a number of two dimensional diagrams, but since there are only four lead isotopes, it follows that two sets of two ratios including all isotopes give all the available information. The picture loses clarity when large numbers of points are plotted on the same diagram. For example, the visual comparisons of large number of lead isotope data measured for artefacts with many ores can get quite complicated. It is therefore useful, in the first instance, to delineate an area on the diagram, which encloses the data points of lead isotope measurements of all different ore samples from a particular ore deposit, this area can be described as the 'lead isotope field' of that deposit and used for comparisons with archaeological artefacts. Our initial approach (e.g. Stos-Gale et al. 1986) was to plot the data for the three isotope ratios involved on two diagrams and

to draw an envelope around the error bars of the outlying data. Because of the correlations normally inherent in lead isotope data (resulting in part from the constant ratio of lead's parent terrestrial uranium isotopes - see Chapter 4), it is strictly incorrect to plot orthogonal 2σ error bars for each point in a two dimensional plot of lead isotope ratios. Instead error ellipses should be plotted for each point (Ludwig 1980, p. 6-7). For the totality of lead isotope ratios measured for one ore deposit a confidence ellipse (at, say 95% confidence level) can be calculated. The use of such confidence ellipses to describe an assemblage of lead isotope data for an individual ore deposit, "... particularly when comparing populations from different ore bodies and prospects ...", has been described by Gulson (1986). The construction of such confidence ellipses depends on the assumption of bivariate normality for the data used, therefore each set of data is checked for normality using the BMDP 2d statistical software. It has been demonstrated in the previous paragraph that all lead isotope data on ores accumulated so far fulfil this condition. It is not necessary then to use the errors for the individual data points, because the ellipses calculated for each such group of points automatically include both the analytical and the geological variability.

Since 1988 we have all our lead isotope data stored on IBM computers in a PARADOX (Borland) database. The lead isotope data from this program can be directly transferred to our own computer graphics program (PICTURE, Antoniuk and Stos-Gale 1987) which plots two-dimensional diagrams of the data points. For each ore deposit it is possible to calculate within the PICTURE software a confidence ellipse at a chosen statistical confidence level. As has been mentioned above, each deposit should be characterised by at least 20 geologically well selected ore samples. For fewer samples, it is possible to use F-tests and Hotelling's T tests, but the true extent of the fields and proper assessment of overlapping will remain uncertain. A number of ellipses for the more important ore deposits and sets of data are kept on a computer and each new set of data

can be directly compared visually with the whole range of ore deposits.

The group in the Smithsonian Institution has another approach to plotting bivariate lead isotope ratio diagrams, with ellipses drawn at preselected confidence levels, using its own programme RAPLOT published within the Brookhaven multivariate statistical software (Sayre 1975); this programme is now also available for IBM PC compatible desktop computers.

Yet another approach was suggested in recent years by Reedy and Reedy (1988) who advocated use of the fractional atomic abundances (direct concentrations adding up to 1) of the four isotopes of lead ^{204}Pb, ^{206}Pb, ^{207}Pb,^{208}Pb, which they claim to be less correlated than the ratios (one must in fact choose only three of these fractional abundances; they are not completely independent, their sum being unity), rather than lead isotope ratios. In fact, their analysis shows rather marginal differences between the correlations for atomic abundances versus ratios, but there is a more fundamental reason for choosing ratios. All mass spectrometers used for accurate isotopic work in geochemistry or archaeology produce their primary data as ratios, for technical reasons partly connected with the techniques used for correcting for fractionation during an analysis (Dodson 1963); all lead isotope data in the literature have been produced as ratios. So far the majority of lead isotope data produced for archaeology have been obtained using single collector mass spectrometers where the ion beams for the different isotopes were switched rapidly and sequentially into the collector. Unavoidable instability in the thermal ionisation process forced the data to be obtained as ratios of ion beam currents, with interpolation procedures to take account as far as possible of the time varying ion currents (Webster 1960, Dodson 1963, Wasserburg et al. 1969, Wasserburg 1987, 134-138). Modern mass spectrometers sometimes have software which allows the data to be printed out as fractional atomic abundances, but these data are secondary, having been computed from the directly measured ratio data.

In practice, it seems to make little difference whether one uses the ratios we select, another choice of ratios, or the atomic abundances. Empirical investigation of the effect of such alternative choices of input data for the BMDP programme 7M (discriminant analysis) and the Brookhaven programmes RAPLOT, CONDIST, ADCORR and ADSEARCH, finds no differences, within computational error, between the computed probabilities and other statistical parameters, which result from the different choices of input data type. Sayre (personal communication) reports the same conclusion.

Figure 25 shows 90% confidence level fields, produced using the programme PICTURE, for some copper ore deposits listed in Tables 3 and 4 including most of those in the Aegean and the Central and Eastern Mediterranean. The large extent of the isotopic field for Timna is due to the presence of uranium in some of the copper ores there, so that evolution away from the isotopic composition at deposition has continued until the present day. On this diagram, the need for using all three lead isotope ratios is clearly demonstrated; for example, the overlaps visible in the upper diagram of Figure 25 between Kythnos and Cyprus, and Essimi with Cyprus, vanish in the lower diagram.

The most common lead isotope ratios for the ore deposits investigated for this work are in the region of the $^{208}Pb/^{206}Pb$ values of 2.06 to 2.08. Within this range of lead isotope ratios lie many fingerprints of the lead/silver/copper deposits of Europe and the Near East. In the cases of close similarities, a statistical method is needed to assign probabilities of the lead isotope data for one ore deposit falling into the isotopic field of another deposit, and for estimating the probability that the isotopic composition of an artefact assigns it to one ore deposit rather than another. Only in this way it is possible to combine all three isotopic ratios together in some form of multivariate statistical analysis. When dealing with specific ore samples collected on geological field trips, it is known in advance that each geologically well defined ore deposit constitutes a

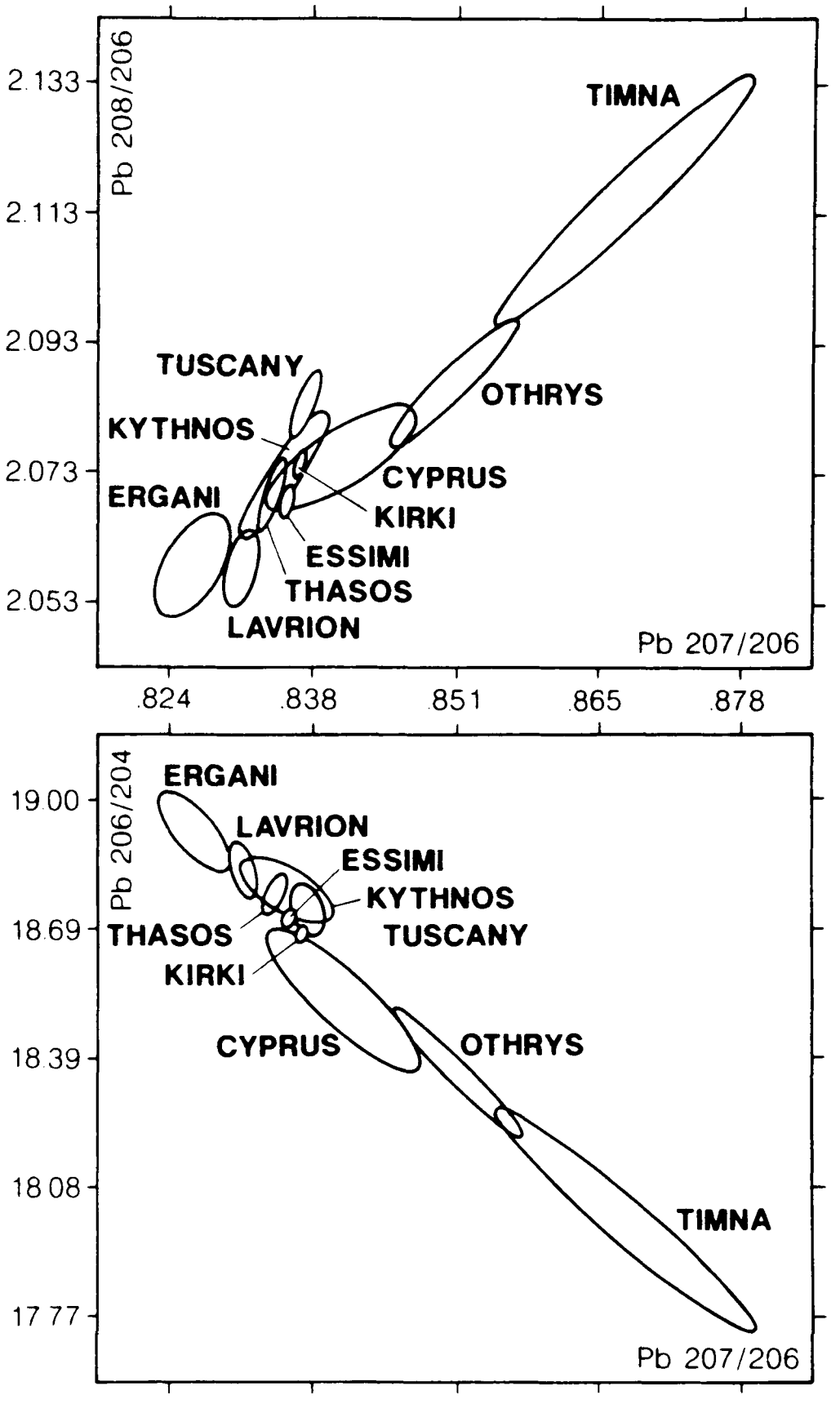


Fig. 25. General lay-out of the Mediterranean copper deposits. Some of the fields which seem to overlap on the upper diagram are clearly separated on the lower.

group for statistical purposes. For this reason, the basic ore field groups are defined by the geological origin of samples and to discriminate between the groups discriminant function analysis is appropriate.

6.5. Discriminant function analysis of lead isotope data.

The discriminant function analysis seeks an answer to the question of how well it is possible to separate two or more groups of data points, if there are available measurements of several variables characteristic for these points. The lead isotope data measured for the ore samples and archaeological artefacts consist of points in three-dimensional space; the three independent lead isotope ratios characterise the exact position of these points. The most appropriate, readily available, software package which calculates the linear discriminant functions of groups of data is the BMDP 7m Stepwise Discriminant Analysis Programme. The form of data for discriminant analyses of groups characterised by their lead isotope ratios is a table with four variables: three independent lead isotope ratios and the origin, meaning the geographical origin of the minerals, or origin assigned to an object by its archaeological or other context. The BMDP 7m programme calculates the mean variance and covariance of each group, and then the Mahalanobis distance defined as:

$$D_i^2 = \sum_{r=1}^{p}\sum_{s=1}^{p} (x_{r_i} - x_{r_j})\, c^{rs}\, (x_{s_i} - x_{s_j}) \qquad (6.1)$$

where c^{rs} is the element in the rth row and sth column of the pooled sample covariance matrix (Manly 1986).

The observation is then allocated to the group for which D_i^2 has the smallest value. The BMDP 7m calculates also the Wilk's λ for each group of samples, and carries the classification of cases into groups. Following these operations a table is listed for each of the groups giving the Mahalanobis D^2 and posterior probability. In this way a probability of group membership is

calculated for each sample.

In the second part of this program canonical discriminant functions are calculated. The canonical discriminant functions of a group of variables are determined in order to separate them into groups as well as possible. The simplest approach involves taking for this purpose a linear combination of the X variables:

$$Z = a_1 X_1 + a_2 X_2 + ... + a_p X_p \tag{6.2}$$

Groups can be well separated using Z if the mean value changes considerably from group to group, with the values within the group being fairly constant. A way to choose the coefficients $a_1 ... a_p$ in the index is to maximise the ratio F of the mean's square M_B between groups and M_W within groups. Therefore a suitable function for separating the groups can be defined as the linear combination for which $F = M_B/M_W$ is as large as possible. Using this approach, it is possible to determine several linear combinations for separating groups. They are referred to as canonical discriminant functions. The first function Z_1 gives the maximum possible F ratio on a one-way analysis of variance for the variation within and between the groups. The canonical variables are calculated by BMDP 7m and plotted on multivariate diagrams which show in a graphic form the separation between the groups and individual samples.

Figures 26, 27, 28, 29 and 30 show multivariate plots of some of the lead isotope signatures of the metal deposits which do not separate very well on the bivariate lead isotope ratio plots. Figure 26 shows the separation of the Aegean galenas from different occurrences which on the bivariate lead isotope diagram (see Figure 15) heavily overlap over each other. The comparison of these two figures (15 and 26) shows very clearly the advantages of using stepwise

discriminant analyses in the presentation of the lead isotope data. On present evidence, however, some of the ores from Chalkidiki and the island of Thasos have indistinguishable lead isotope composition.

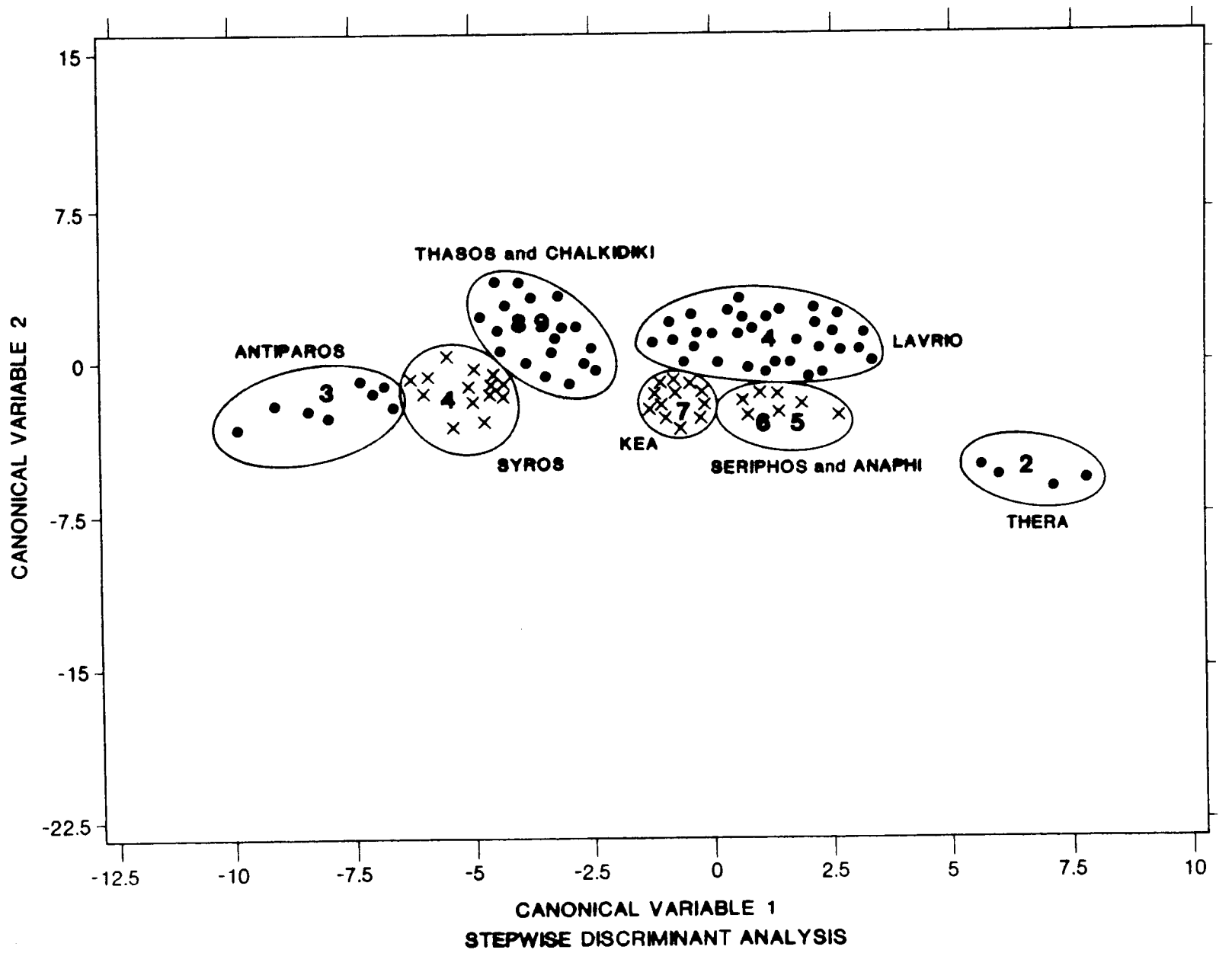
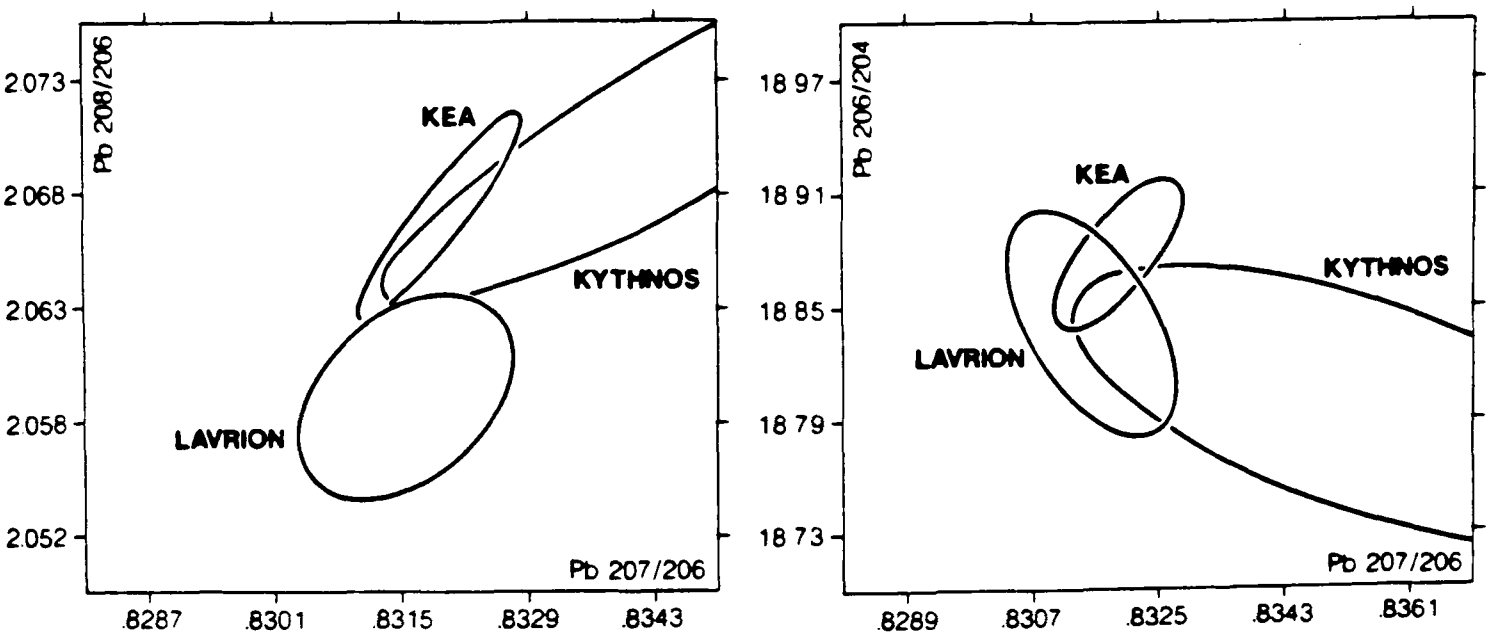


Fig. 26. Stepwise discriminant analysis of lead isotope data of the Aegean galenas and copper ores from different locations.

Figure 27 shows a 'close-up' illustration of the graphical effects of the BMDP scatter plots used to demonstrate statistical separation of the ore fields. Three groups of minerals from the Aegean, galena from Kea, copper slags and ores from the island of Kythnos and the various minerals from the multimetallic deposit of Lavrion overlap partially on the bivariate plots. The discriminant analysis of lead isotope data provides very clear separation of those three fields.

Figure 28 shows another set of results of the stepwise discriminant analysis on several groups of Greek and Turkish ores falling very closely together



STEPWISE DISCRIMINANT ANALYSIS

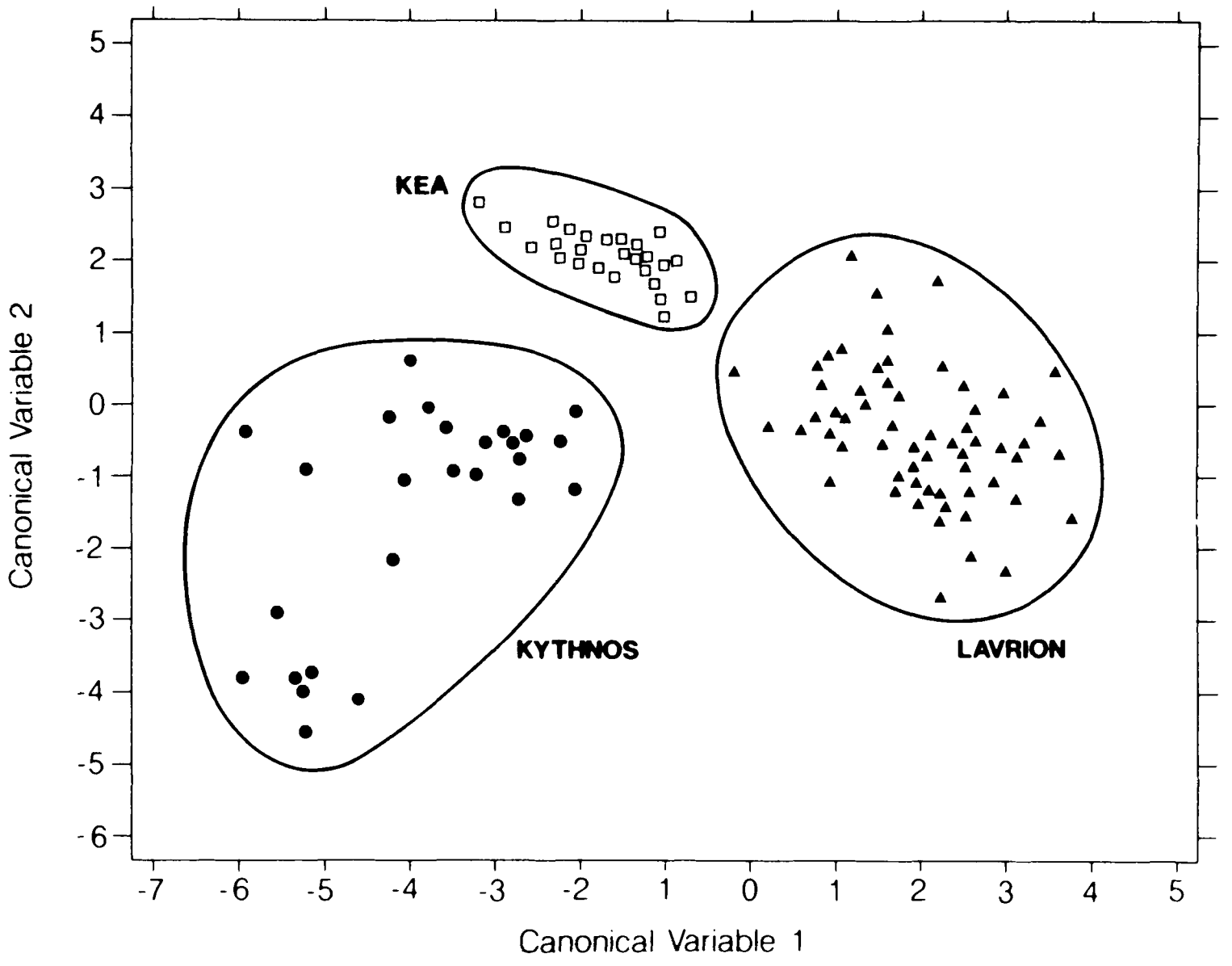


Fig. 27. Lead isotope 'fingerprints' of the ore and slag samples from Kea, Lavrion and Kythnos. The upper part of the drawing shows the bivariate plots of ellipses drawn around the lead isotope data points, the lower shows discriminant functions calculated for the same data points.

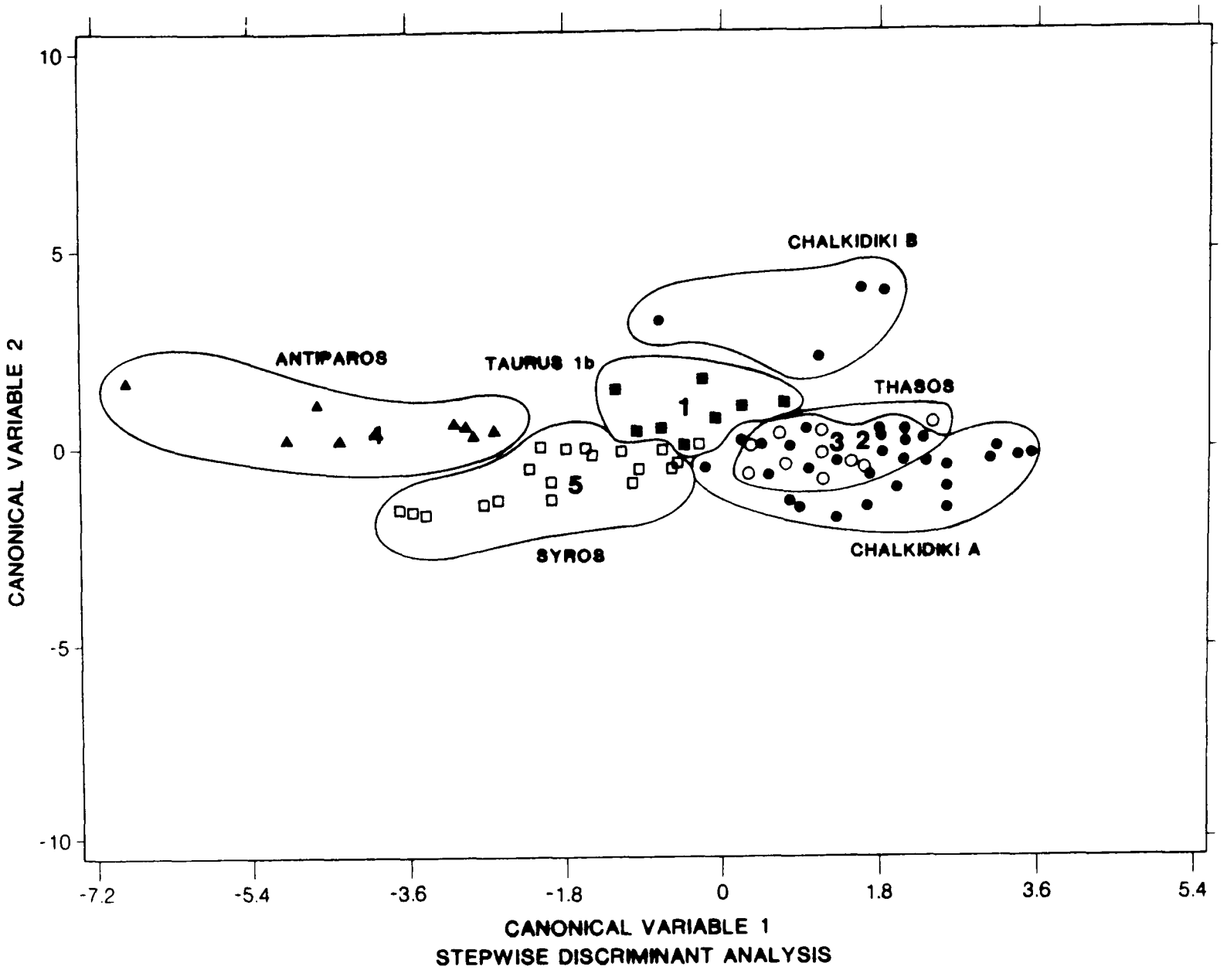


Fig. 28. Scatterplot of discriminant functions calculated for several overlapping lead isotope 'fields' of the Mediterranean copper and lead ores.

on the bivariate lead isotope diagrams. Figure 29 shows discriminant analysis separation of the three Eastern Mediterranean copper sources of the Taurus Mountains in Turkey, Kythnos and Cyprus. Figure 30 shows statistical separation of lead isotope 'fingerprints' of Kythnos and Cyprus and of each with the fields for Essimi and Kirki in the Rhodope Mountains in Northern Greece. All those deposits, excluding only Chalkidiki and Thasos, can be statistically separated, both graphically using the illustrated scatterplots and by the numerical data generated by BMDP 7M.

Statistically speaking, a good separation is obtained between two ore deposit lead isotope fields when the numerical probabilities of all the samples from one field belonging to a nearby field are less than 0.5 (which means 50%).

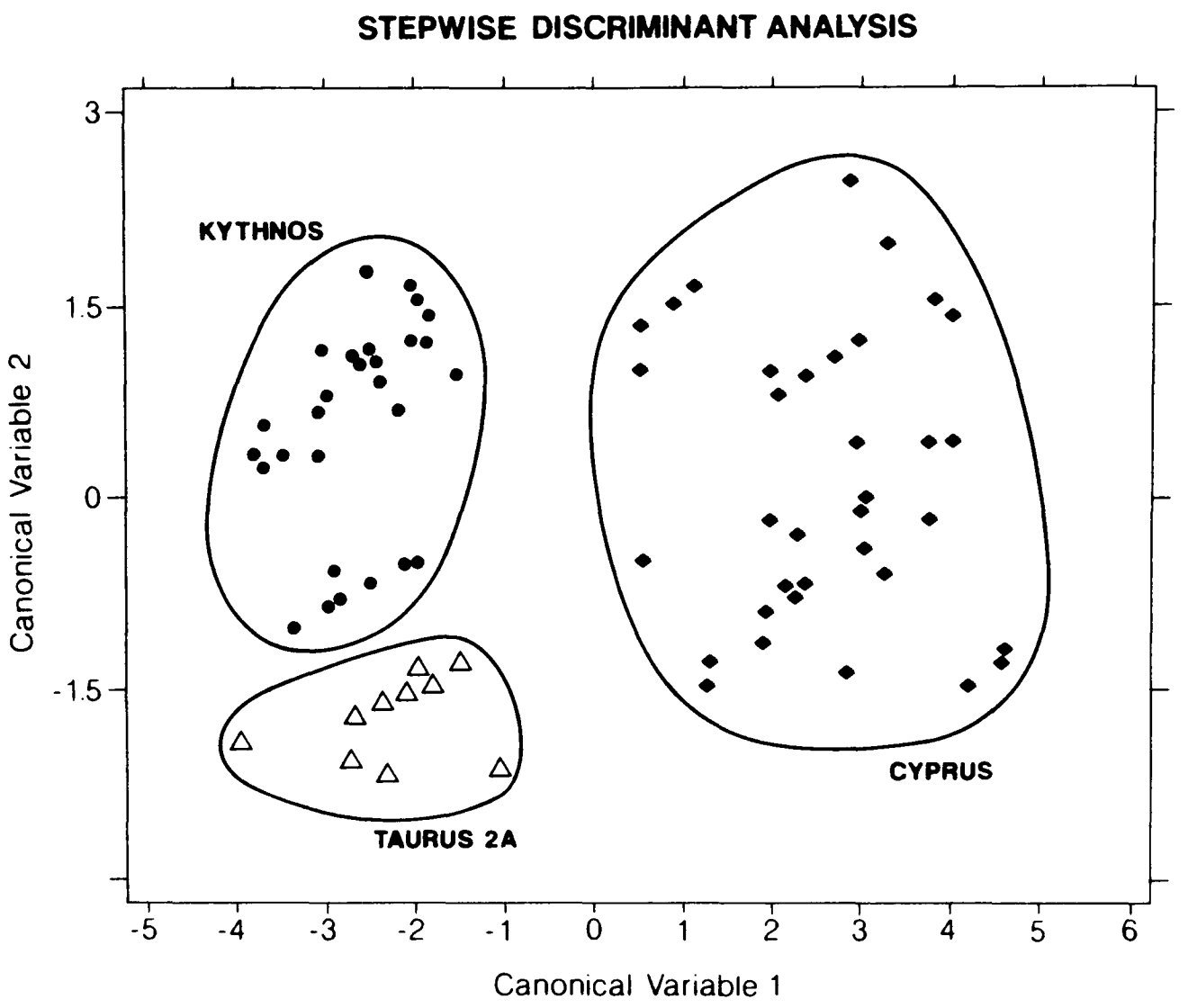


Fig. 29. Scatterplot of the discriminant functions calculated for lead isotope data of ores and slags from Kythnos, Cyprus and Taurus Mountains.

The enclosing lines drawn around samples from the same ore deposit are merely to guide the eye; they have no statistical significance.

6.6. Requirements and limitations for statistical analysis of lead isotope data of ore samples.

Every year there are more lead isotope data on ore deposits relevant to archaeometallurgical provenance studies published by various groups, and invariably the data is then used by all interested for interpretation of the origin of metal artefacts. For example, the Turkish ore deposits are very important in archaeological provenance studies of metals in the Bronze Age, because some of the earliest metallurgical processes, such as the introduction of tin bronze, might have originated in this part of the world. Scholars have often suggested that the knowledge of metallurgy developed first in the Near East and then spread through Anatolia to South-Eastern Europe. As has been mentioned

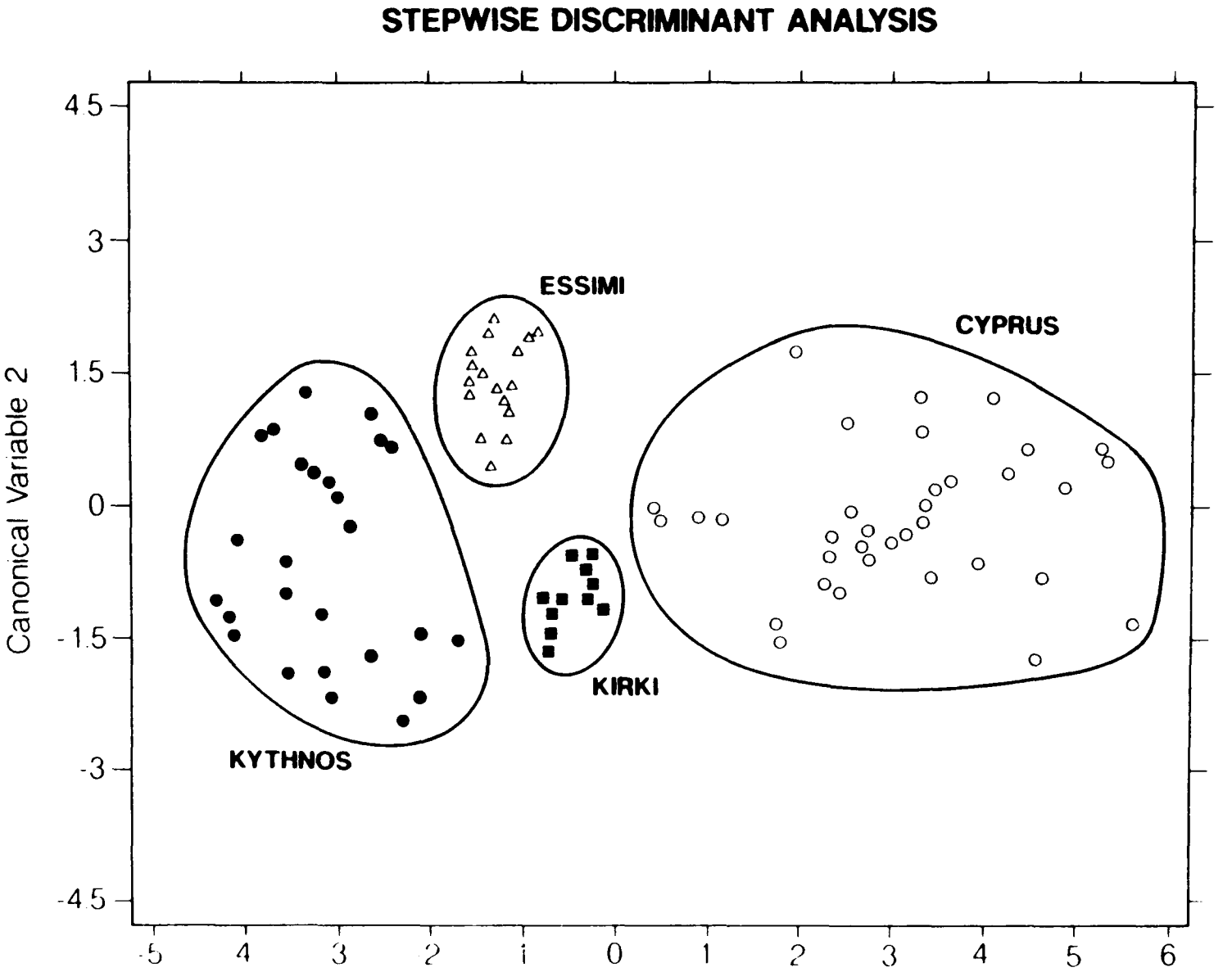


Fig. 30. Scatterplot of the discriminant functions calculated for ore and slag samples from Kythnos, Cyprus and the Rhodope Mountains.

earlier, although quite substantial geological fieldwork has been carried out in Turkey by the team led by Günther Wagner, (Wagner et al. 1989 and references therein), there are currently only about 160 lead isotope analyses published for these deposits, many of which are lead rather than copper deposits.

The Turkish/American team directed by Aslihan Yener has also published lead isotope data for ore deposits in southern Turkey (Taurus Mountains). This is another extremely important archaeometallurgical area, even more so now, since Yener (1989) published her findings of tin smelting in these mountains. Unfortunately again, the choice of samples analysed for their lead isotope composition seems strange (very few copper ores; isotope groups are formed from lead isotope data of single samples of minerals collected in valleys distant from

each other) and totally insufficient for any meaningful lead isotope characterisation of the area (Yener et al. 1991, see also comments in Archaeometry 2/1992).

A typical example of such unfinished (as it seems at present) work is the assemblage of lead isotope data from the deposits of North West Turkey. This geographical region is of great importance in archaeometallurgical research, because it is possible that the earliest metallurgical developments came to the Aegean from this direction. The whole of Northern Turkey is very rich in lead, silver and copper ore deposits (Wagner et al. 1989) and it seems vital that this area should be carefully characterised isotopically. Three publications contain good geological and field descriptions, and some lead isotope data of ores from this region (Pernicka et al. 1984, Wagner et al. 1985 and Wagner et al. 1986). With a very few exceptions (for N-W Turkey two analyses were made on samples from each of the localities numbered TG 12, TG 14, TG 142, TG144, TG192 and TG133 and 5 analyses of TG 18) all published analyses are single measurements for each occurrence. Mineralogically, the samples analysed are a random (as it seems) selection of galenas, copper minerals and lead or copper slags. Because of the importance of this area in the metallurgical history of Europe, the data, scarce as it is, is often used for comparisons with ancient objects (Yener et al. 1991, Pernicka et al. 1984, Stos-Gale 1992). There seems to be no reason not to use these data as a general indication of the composition of the ores from the Troad peninsula. However, the selection of samples and the few isotopic analyses preclude any meaningful statistical analysis and any certain conclusions.

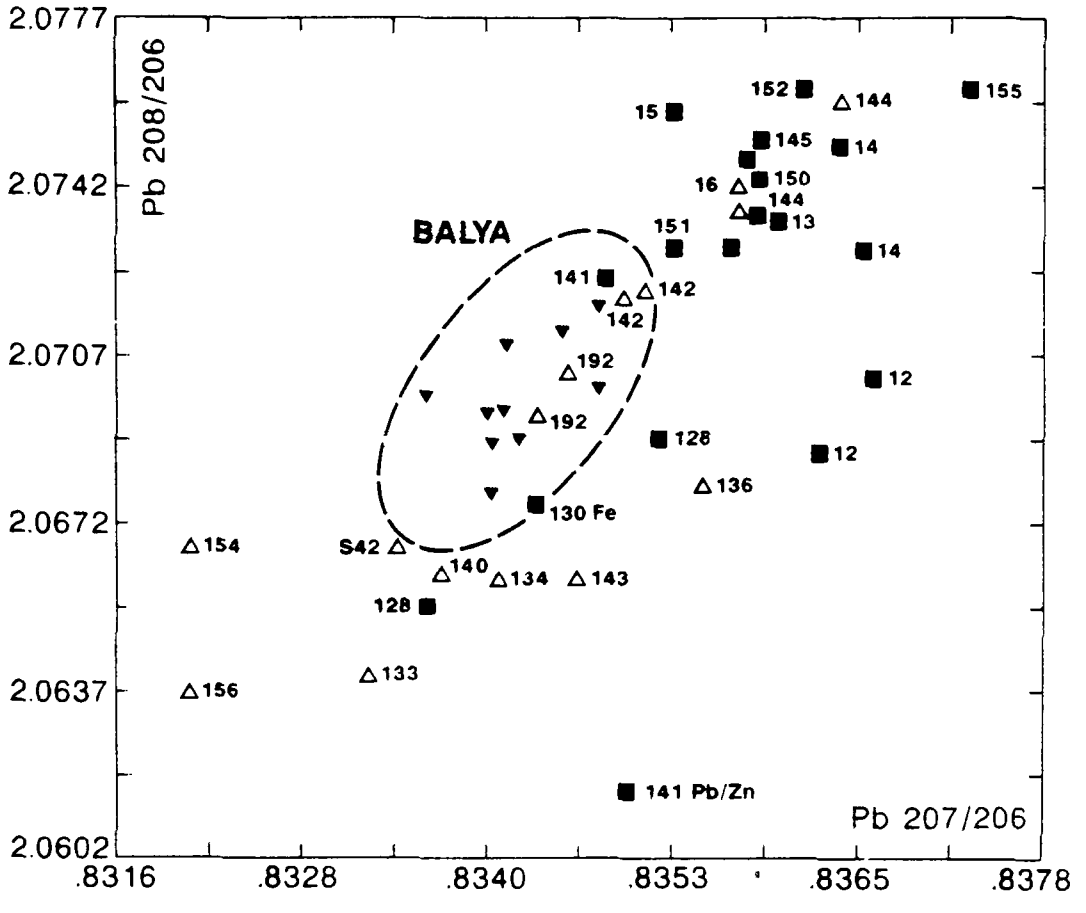
The Mainz lead isotope data for ore deposits in North West Turkey are plotted in Figure 31 and the names of the mines, together with comments on their antiquity and type of the mineralisation compiled from all relevant Heidelberg/Mainz publications, are listed in Table 5. The Troad peninsula is divided administratively between the provinces of Balikesir and Canakkale and Bursa is the next province to the east from the Troad. The Serceorenkoy mine in Balikesir

(TG 192) is situated in the East of the Province of Balikesir and geographically perhaps stands separately from all the other deposits in the two administrative regions of the Troad.

Table 5. Turkish ore deposits surveyed by the Heidelberg-Mainz group.

German No.	Site	Province	Minerals	Archaeology
TG12	Altinoluk	Balikesir	Pb, Ag	Byzantine
TG128	Avcilar	Balikesir	Pb	Greek/Roman
TG13	Handeresi	Balikesir	Pb, Ag, slag	None
TG130	Gurekoy	Balikesir	Fe, slag	None
TG14	Karaaydin	Balikesir	Pb, Ag	Hellen./Byzant.
TG142	Kozcagiz	Balikesir	Cu, slag, Pb	Medieaval
TG143	Maden Adasi	Balikesir	Pb, Cu	Medieaval
TG144	Halirar	Balikesir	Pb, Cu	None
TG145	Kuserlik	Balikesir	Pb, slag	Greek/Roman
TG152	Mentesdere	Balikesir	Pb	None
TG192	Serceorenkoy	Balikesir	Cu	Prehistoric
TG153	Madenbelenitepe	Bursa	Pb, Zn, Tin?	17th cent AD
TG154	Keles	Bursa	Cu, slag, Pb	None
TG156	Tahtakopru	Bursa	Cu, slag	16th cent AD
TG133	Dogancilar	Canakkale	Cu, slag	Greek/Roman
TG134	Kocayayla	Canakkale	Pb, Cu	None
TG136	Kocayayla	Canakkale	Cu slag	Medieaval
TG138	Yuvalar	Canakkale	Cu	Greek/Roman?
TG139	Yuvalar	Canakkale	Cu slag	Greek/Roman?
TG140	Dagoba	Canakkale	Pb, Cu	None
TG141	Kustepe	Canakkale	Pb, Zn	None
TG146	Bakirgac	Canakkale	Pb	None
TG147	Kiracoba	Canakkale	Pb, Ag	None
TG15	Gumusler	Canakkale	Pb, Ag	None
TG150	Arapucandere	Canakkale	Pb, Ag	Greek/Roman
TG151	Bekten	Canakkale	Pb, Ag	Hellenistic
TG16	Kurtasi	Canakkale	Pb, Cu	None
TG17	Sofulur	Canakkale	Pb, Cu	None
TG155	Gumuskoy	Kutuhaya	Pb, Ag	Prehistoric

Apart from the tight group formed by the lead/silver ores of Balya (TG 18), all other data are scattered in a large portion of isotopic space. It is very probable that many analyses of ores from each of the occurrences would produce a picture similar to our Cypriot or Tuscany field; some of the mining regions might have indistinguishable compositions (i.e. TG144, TG146, TG150 etc.);



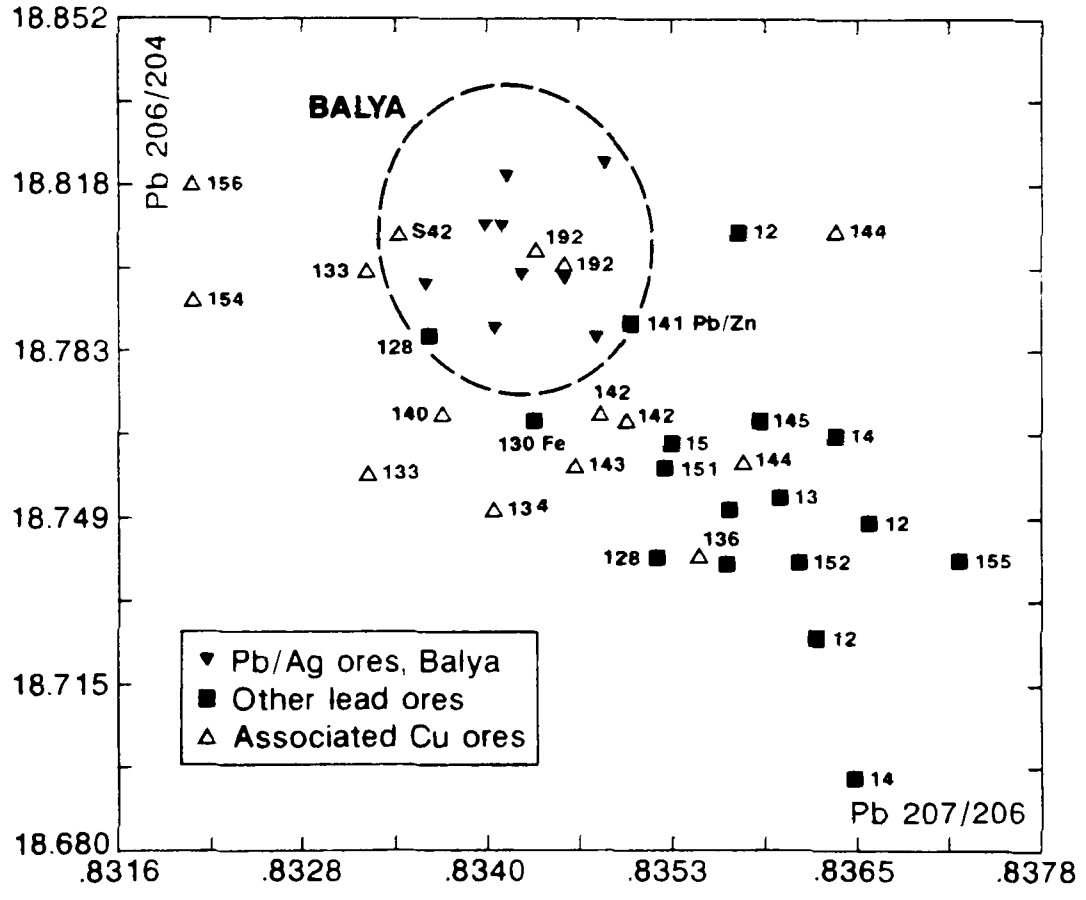


Fig. 31. Lead isotope ratios of Turkish ores published by the Heidelberg-Mainz group.

others might be quite separate (see for example how the pairs of samples from TG12 and TG14 separate on the upper diagram. The eastern copper mines TG154 and 156 very probably have quite distinct lead isotope signatures. As a first step in making the most of these tantalising data it can be suggested that all the samples coming from outcrops where there is no indication of any ancient exploitation can be removed, and then the lead ores (which mostly plot in the right hand side of the diagram) can be only used for point-by-point comparison with single artefacts and even perhaps some sort of 'Troad' lead isotope fields can be constructed with an estimated probability of the possible range of compositions. All these approaches will not, however, provide sound ore lead isotope signatures for provenance studies of, say, Bronze Age artefacts, because from the field descriptions it seems that only some of these deposits have the potential to be of any importance in the Bronze age. For copper the most likely candidates are the deposits in Bursa (TG 154 and 156), the mines in Dogancilar (TG133, for discussion see Stos-Gale et al. 1989) and the mine of Serenceorenkoy (TG192), for silver Balya (TG18) and Gumuskoy (TG155). It is clear from this scatter plot that the distribution of all these data is not normal. With some imagination it might be possible to divide the data into three groups: Balya, Troad A (12, 13, 14, 144, 152, etc. clustering in the upper right hand corner of the 208/206 diagram) and Troad B (140, 133, 128, etc in the lower left hand corner of the 208/206 diagram). However, there is no reason to assume that they belong **geologically** to the same group and therefore creating such groups of lead isotope data and calculating their mean values as correct for the 'Troad' is, from the geochemical point of view, meaningless.

Some previous attempts at grouping deposits in the Troad have been published in the last two years. Slightly different groups were formed from the German data by Sayre (Yener et al.1991) and myself (Stos-Gale 1992b). In both cases, the division was made not on geological grounds, but purely by

associating together ore and slag samples which have similar lead isotope ratios. In retrospect, there seems to be too little geological information to provide a sure geological basis for forming these two 'fields'. Each group consists of over 8 different deposits, mostly with one analysis each, linearly distributed over a distance of about 100 km. My approach was to look for ore deposits where copper ores were mostly associated with lead ores, because the copper archaeological objects under investigation (from the Early Bronze Age site on the island of Lesbos) had an unusually high lead content which seemed to indicate primitive copper smelting from such ores.

Finally, one cannot exclude the possibility that some ore deposits will be isotopically indistinguishable. So far only one serious overlap has been found amongst the ores listed in Tables 3 and 4, apart from the data on ores from the island of Thasos and the Mainland multimetallic deposit on the Chalkidiki peninsula (see Figure 12b). Perhaps this should be set in context, by noting that copper ores are insignificant in amount on Thasos and that the T.L. (thermoluminescence) date obtained for a copper slag heap there at Makrirachi is 260 ±160 B.C. (Pernicka and Wagner 1988, 229). Additionally, it seems that copper on Thasos was not smelted in the Bronze Age because our lead isotope analyses of a series of Late Bronze Age bronze objects excavated on Thasos show that all metal originated outside this island (Gale and Stos-Gale 1992). This sort of evidence, that in the period under review the local people did not exploit their own meagre resources and that therefore the resource in question cannot have been used abroad in that period, provides admissible extra evidence in the rare cases where partial overlap of ore source lead isotope compositions prevents more direct conclusions. Similar criteria can be used for the Kythnian lead isotope 'fingerprint' discussed earlier, which, for the time being, seems to be relevant only to the copper artefacts dated to the Early Bronze Age, because the slags and ores used to construct it come from a site which has been dated

only to this period (Stos-Gale 1989).

It is of course important to realise that, if the lead isotope analysis of a copper artefact results in an isotopic composition which falls within the isotopic field of a particular copper ore deposit, then strictly one can say only that the copper of the artefact is consistent with having come from that ore deposit. In this regard all provenancing techniques are on an equal footing. On the other hand if, say, the lead isotopic composition of a Minoan copper alloy artefact falls well outside the Cypriot field, it is certain that the artefact was not made of Cypriot copper. In this respect Yener et al. (1991) have recently put doubts as to the limitations of the lead isotope ratios for any deposit by finding in our published data 'outliers', for example for Cyprus and Lavrion (already mentioned in Chapter 5). Since the exhaustive geological work by Gulson (1986) and others on ore deposits has not shown this (save for rare copper deposits containing uranium) the 'outliers' might just be erroneous analyses (sample mix-up, forced mass spectrometric runs of poor accuracy, etc.) To check this possibility the analyses of the so called 'outliers' were repeated; as mentioned in the previous chapter, the new data fall within the 90% confidence ellipse defined by the core group of analyses. It seems therefore, that at present there is no empirical evidence that the lead isotope compositions of any metal ore deposit include highly deviant outliers, and there is no geological reason to expect it.

In conclusion, all evidence so far available from lead isotope analyses of ore deposits points to the possibility of a very good chance of finding the exact geographical origin of a mineral used in the production of an ancient artefact. The most important points can be summarised as follows:

1. The differentiation of lead isotope characteristics of ore deposits in different geographical locations is sufficient to provide 'fingerprints' for lead isotope provenance studies to the point not only of the exclusion of cer-

tain ore deposits as metal sources, but also for identification of the source with a high probability.

2. This, however, can be achieved only if provenance studies of metal objects, pigments or other mineral based materials are conducted in parallel with analytical and geological fieldwork in the deposits relevant to a given project.

3. The lead isotope evidence might sometimes point to more than one ore source from which the material of the archaeological object derives. However, with a sufficient number of lead isotope analyses of the ores, it is always possible to calculate the probability of its derivation from each of the sources.

4. The accumulated lead isotope data-base on ores from individual regions can serve as a data-base for many different projects.

6.7. Restrictions of lead isotope provenance studies of archaeological metal artefacts.

In the previous paragraphs I have discussed the lead isotope signatures of metal ore deposits. The possibility of distinguishing between ores from geographically different mineralisations means the possibility of distinguishing between metals made from ores from those different localities. In Chapter 5 it was pointed out that this simple interpretation is possible only if each of the metal artefacts was made from material originating from just one ore source. In certain cases such assumptions cannot be sustained, because of the large quantity of metal in circulation and the many different ore sources which might have been used: it is possible that most metals would have been made from an assortment of pieces of metal which originated from different mineralisations. Some are doubtful if this method is suitable for metals later than the Bronze Age (i.e. later than approximately 1000 BC). Such predictions can be only checked experimentally. It seems quite possible that at least in some cases in later history the number

of metal sources used in a certain region at a certain time was quite limited. In such cases even if the re-melting was common, the pattern of the ore sources can be still visible, even if distorted to a certain extent.

The problems of mixing of metals of different origin in the Bronze Age period is worth a closer consideration in the light of the known patterns of lead isotope fingerprints of ore deposits. Unfortunately, as shown by analyses in Percy (1861) there is no way of predicting the **amount** of lead from a given ore deposit which might have remained in the copper metal after smelting. Our numerous elemental analyses of the Bronze Age artefacts from the Mediterranean (more than 2,000 artefacts) show clearly that in a great majority of cases the lead content in copper-based metals is found in concentrations well below 0.5%. It is generally true that copper made from Cypriot ores (we have analysed over 100 LBA ingots produced on this island) is very low in lead (usually around 100 parts per million). On the other hand, copper metal smelted from ores found on some of the Cycladic islands, where copper ores are associated with lead ores (Stos-Gale 1992b), can be very high in lead. Since the amount of lead present in the final metal depends not only on the association of copper ores with other minerals, but also to a considerable degree on the technology of metal smelting, metal produced from ores of the same deposit can have strikingly different chemical composition.

The possibilities of different lead isotope compositions resulting from such mixing are endless. Depending on the lead concentration in the metal of each scrap piece and the proportion of the different scrap pieces in the resulting melt, the lead isotope composition of the final object on each of the bivariate lead isotope diagrams will be anywhere between the original compositions. On the other hand, when analyzing groups of objects from the same archaeological site and the same stratum one can expect to notice if there is a 'mixing' pattern. For example, if the metal was coming from two isotopically different sources then a

scatter of the lead isotope compositions of different objects should occur along the lines joining the values characteristic for the 'mother' deposits. So far, our lead isotope data for archaeologically uniform (i.e. the same site or geographical area and period) groups of objects from the Mediterranean Bronze Age do not show any strong 'mixing' patterns. There might be several explanations of this result. The most important, perhaps, lies in the early technology of the individual metal smith. The metallurgical operations of casting and repairing of broken objects were mostly carried out in the settlements. The smith used small crucibles (typical excavated crucibles are no larger than 20 cm in diameter) and typically only small amounts of metal would be melted to cast a dagger, several pins or tweezers, etc. For such small operations the selection of scrap metal in all probability was careful: the most economic way of casting a new object from scrap metal would be through the selection of pieces of scrap matching the size of the intended object. If such selection was used, then the lead isotope signature of the original would be carried on to the new artefact and still reflect the actual source of metal used. The number of metal sources used in the Mediterranean Bronze Age seems quite limited, and in fact in the Late Bronze Age there are fewer of them than in the earlier periods.

The exhaustive lead isotope analyses of the Late Bronze Age copper ingots show conclusively that there was no mixing of metal at that stage (Gale 1991). However, the problem of 'mixing' of metal used in the production of ancient artefacts is a real one, and always should be taken into account when interpreting lead isotope data.

B. SOLVING ARCHAEOLOGICAL PROBLEMS BY LEAD ISOTOPE STUDIES.

7. APPLICATION OF LEAD ISOTOPE PROVENANCE STUDIES FOR ESTABLISHING SOURCES OF METALS AND TRADE CONTACTS OF MINOAN (3000-1000 BC) CRETE.

7.1. The role of Crete in the Bronze Age Mediterranean and the importance of the trade in metals.

"... Out in the middle of the wine dark sea there lies a land called Crete, a rich and lovely land, washed by the waves on every side, densely peopled and boasting ninety cities. Each of the several races on the isle has its own language...One of the ninety cities is a great city called Cnossus, and there, for nine years King Minos ruled and enjoyed the friendship of almighty Zeus." (Odyssey, XIX, 172-179).

This and other similar passages from Homer's **Odyssey** and **Iliad**, the story of the siege and capture of Troy by the Greeks, for centuries have fired the imagination of educated Europeans. It can be said that these two volumes constitute the first expression of the Western mind in literary form. The vivid description of people and places in this epic inspired Schliemann to search for Troy and, later, to search Greece for palaces of the Homeric heroes. Schliemann's archaeological excavations proved for the first time that long before the Romans and Classical Greeks there was in the Mediterranean an essentially European culture equal in its material culture to the achievements of Egyptians and Assyrians. The earliest remarkable cultural, technical, social and artistic developments took place in the 3rd millenium BC on the island of Crete.

Owing to its location on the crossroads of the eastern Mediterranean the island was exposed during its history to the most varied influences from many cultures. Bengtson writes (1988, 8): " ...Like a concave mirror, Crete united

many beams into a powerful beam shining with a strong light through the darkness of the early period of the Aegean history." This view might be changing slightly as a result of new excavations in the Cyclades and the Northern Aegean, but there can be no doubt that Crete must have played an important role in the trade network of the Aegean since the Early Minoan times (see Table 6 for chronology).

Obsidian and metals must have been amongst the earliest raw materials which were imported to Crete. It seems at present most likely that the earliest developments in metallurgy in the eastern Mediterranean took place in metal rich areas of the Anatolian Plateau. Small pins, punches (awls) and axes made of copper, sometimes with small amounts of arsenic, are the first metal objects found in the early 3rd millenium BC context in Greece. It is generally thought that these first metal implements did not really show much superiority over their bone and stone equivalents. The real break-through in the quality of copper-based metal came with the widespread production of arsenical copper and later (at the end of the EBA) with the introduction of tin bronze. The polymetallic technology in the Eastern Mediterranean developed on a large scale at the end of the 3rd millenium BC (Branigan 1968). It seems that daggers and short swords were the first metal objects which did not have their predecessors in stone. The large number of these weapons found in early and Middle Bronze Age sites across the Eastern Mediterranean indicates that there was a prolific and de-centralized production of these weapons. The earliest daggers of distinct types were made in the Near and Middle East, Crete, Cyclades and Cyprus. Large deposits of copper are known in Anatolia and Cyprus. Also there are two deposits in the Near East which have been archaeometallurgically studied: Feinan in Jordan and Timna in Israel. Timna is a deposit exploited mainly in the Late Bronze Age and with clear contacts with Egypt (Rothenberg 1988). The copper mines of Feinan are of much greater importance and the vast copper slag heaps prove

that the amount of metal smelted from the ores at various times in the past was very large (Hauptman 1989). The production of copper in Feinan started in the Chalcolithic period and even if the archaeological evidence on the site does not indicate any contacts with the Mediterranean, some of this metal might have traveled there. The amount of copper ores on the Cycladic islands is not as large as at the other geographical areas mentioned above, but it is known that copper was smelted towards the end of the 3rd millenium BC on Kythnos. There is also some copper on Seriphos (own survey) and small amounts on Siphnos (Pernicka 1989). Which of these deposits were supplying copper for the production of the Early Minoan weapons? Is there a possibility that on Crete itself there are copper and/or silver ores which were exploited in the Bronze Age?

The excavations of Cretan palaces and tombs from the Early, Middle and Late Minoan period produced many metal objects. The majority of these objects are made of high quality copper alloys (arsenical copper in the Early and Middle Minoan and from the early Late Minoan period tin bronze), silver (including several silver daggers unique in the Aegean) and gold. Much of this metalwork has characteristic shapes developed locally. Branigan (1968) published a seminal work on the early Minoan metal finds and came to believe that such early and rich development of metallurgy on Crete must have been based on readily available and cheap sources of metal. The metal artefacts excavated on Crete and in other parts of the Aegean indicate that this island had a leading role in the development of the Aegean metal forms. It was in Crete that the major weapons of the later Bronze Age evolved from Early Bronze Age prototypes, including the double-axe and the 'leaf-shaped' razor (Branigan 1968). A high level of goldsmithing is represented in Middle Minoan examples of filigree and granulation. It seems likely that it was Minoan metalworkers who first produced bronze daggers with inlaid gold and silver design (Luce 1969, Plate XLIII). Such daggers, together with gold, silver and copper vessels, many attested by Ellen

Table 6. Chronology of the Aegean Bronze Age (based on Warren 1992 and Barber and MacGillivray 1984)

Date	Greek Mainland	Cyclades	Minoan Crete
3000 - 2700	Early Helladic I	Early Cycladic I	Early Minoan I
2700 - 2600	Early Helladic I/II	Early Cycladic I/II	Early Minoan I/II
2600 - 2300	Early Helladic II	Early Cycladic II	Early Minoan II A-B
2300 - 2100	Early Helladic III	Early Cycladic IIIA	Early Minoan III
2100 - 1800	Middle Helladic Early/Middle	Early Cycladic IIIB Early/Late	Middle Minoan IA-B
1800 - 1700 c. 1700	Middle Helladic Middle/Late	Middle Cycladic Early	Middle Minoan IB - II Destruction of First Palaces
1700 - 1600	Middle Helladic Late	Middle Cycladic Late	Middle Minoan III
1600 - 1550 c. 1550	Late Helladic I		Early Late Minoan IA Destruction of Akrotiri on Thera
1550 - 1500	Late Helladic I/II	Late Cycladic I	Late Late Minoan IA
1500 - 1450	Late Helladic IIA/B	Late Cycladic II	Late Minoan IB
1450 - 1400	Late Helladic IIB	Late Cycladic III Early	Late Minoan II
1400 - 1300	Late Helladic III A		Late Minoan IIIA
1300 - 1150	Late Helladic III B	Late Cycladic III Middle	Late Minoan III B
1150 - ca. 1000	Late Helladic III C	Late Cycladic III Late/Final	Late Minoan III C

Davis (1977) to be of Minoan workmanship, were found amongst the most advanced and sophisticated hoard of metals of Bronze Age Europe in the Shaft Graves of Mycenae (dated to 16th c. BC).

The leading role of Crete in the development of metallurgical forms and techniques in the Bronze Age Europe brings to mind one important question: what was the mechanism, the driving force behind it? The metals must have been readily available to the Minoans. Was it due to the local development of mining and smelting of metals, or perhaps, at least in part, was the raw material brought across the sea? In this case, how was the trade organised in economic terms: was it a free market economy, or perhaps a Minoan Thalassocracy, as Sir Arthur Evans called the supposed Cretan domination of the Aegean. The idea of Minoan domination of the Aegean became less popular in the last decade (Hagg and Marinatos 1984), but many archaeologists agree with the view expressed by Platon (1987) that the trade in raw materials was 'controlled' by Cretan palaces. However, should the evidence of storage of raw materials in the palaces be accepted as a testimony of the trade controlled by the palace, or just a manifestation of wealth? Perhaps it could be looked at in the same way as the gold in modern bank vaults - not necessary as a raw material for production, but rather as a stored asset and a manifestation of wealth. Nevertheless there is no doubt that Crete was a highly developed cultural and economic centre of the Eastern Aegean world in the 3rd and 2nd millenium BC. How far this dominance and influence went is difficult to assess. Malcolm Wiener (1990 and 1991) in his excellent compilation of all available evidence for the role of Crete at the time of the volcanic eruption of Santorini, in the first phase of the Late Bronze Age (middle 16th century BC - in the accepted pottery-based chronology Late Minoan I), suggests that many of the Aegean islands were in fact part of the Minoan country (I would prefer to call it that rather than the 'Empire'). Consequently he talks about the **isles** of Crete. His arguments are very persuasive,

and therefore the "Minoa" would include Crete, Kythera, Santorini, Rhodes, Melos, Syros and Kea. Those are the islands where there are archaeological sites with Minoan features. However, there are several islands in the immediate neighbourhood of those mentioned above on which no Minoan settlements are known, but because of their geographical position they perhaps also should be included in this group of the "Isles of Crete". These are, amongst others, Seriphos, Siphnos, Kythnos and Naxos.

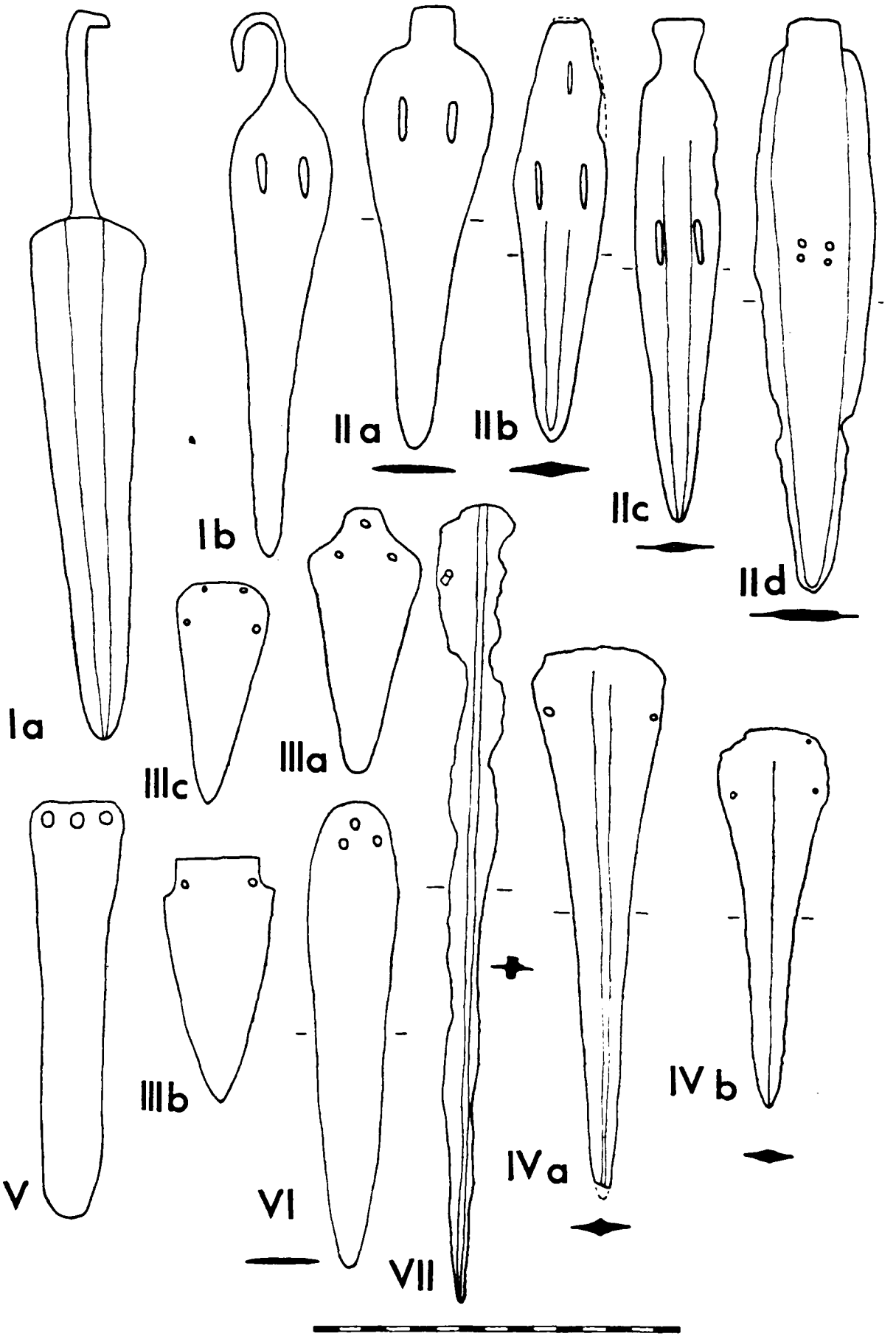
Several hundreds of metal objects from Crete and from the islands mentioned above have been analysed at Oxford in the last ten years. In the first instance many lead and some silver finds from different sites and periods were sampled and analysed. Some of the data have been published (Stos-Gale and Gale 1982 and 1986). Many of the results are still waiting for full publication. The main purpose of this work is to demonstrate the methodology and scope of application of the lead isotope technique for metal provenance studies, rather than to produce an ultimate answer to archaeological questions. Copper is by far the most important metal in the Bronze Age, so it was decided to limit the discussion here only to a comparatively small group of specific copper-based artefacts which have good archaeological typology, and therefore can, with good certainty, be described as Cretan (Minoan) and have been excavated on Crete. On the other hand it would be interesting to investigate similar objects found in the other areas of the Eastern Mediterranean, to see if the same sources of metal were used for similar objects in different areas at the same time. The Bronze Age Minoan weapons - daggers, spearheads and axes - form an ideal group of artefacts to be used for this purpose: the Early and Middle Bronze Age weapons are reliably dated, they were typologically described in great detail by Branigan (1968, 1970 and 1974), and we had a sufficient number of samples (mainly collected in 1983 by Noel Gale from Stuttgart). Additionally, in the Isotrace Laboratory bank of samples there are also examples of many contemporary

weapons from Cyprus (from the collection in Stockholm) and the Cyclades (The British Museum and the Ashmolean Museum, Oxford).

In his seminal work on the beginnings of the Aegean civilization, Renfrew (1972, 319-320) wrote: "One of the problems concerning the development of Aegean metallurgy is to understand why it underwent its tremendous expansion in the Early Bronze Age 2 period ... the appearance of the dagger perhaps presents a clue. For while the Aegean smiths of the final neolithic could make flat axes and awls ... daggers are not seen ... anywhere in Europe until the inception of the Aegean Early Bronze 2 period. In Europe and the Near East, daggers and intensive bronze metallurgy are almost coterminous ... the correlation is an extremely striking one." And further: "... (dagger) makes its appearance in the Aegean in the Troy I period at Troy, Thermi and Poliochni ...."

The lead isotope analyses of the Minoan daggers should at least to a certain degree help to answer this question, if some of the earliest weapons were indeed imported from the northern Aegean or the Near East.

For the Late Bronze Age our collection of samples of Minoan weapons is rather smaller, but it seems sufficient for comparing the metal sources used for the production on Crete of the weapons in the culturally different Late Minoan period. The archaeological evidence from Crete shows a great cultural change on this island around 1500 BC which seems to be connected with violent destruction of the Minoan palaces. The next phase of Minoan culture shows much greater affinity to the mainland Mycenean culture and the meaning of this change is often discussed in the archaeological literature, particularly the question to what degree this might indicate a Mycenean invasion and subsequent domination. It would be interesting therefore to find out if this political change brought also a significant change in the sources of metal used by the Cretan metalsmiths. Lead isotope analysis seems to be an ideal method for solving those problems.



Phot. 5. Shapes of the Early Bronze Age Aegean weapons (after Renfrew 1972, Fig. 16.5.). I - tanged daggers; II - spearheads; III - triangular daggers; IV, V and VI - long daggers; VII - sword.

7.2. Copper deposits in the Eastern Mediterranean and their ancient exploitation.

The development of metallurgy in the 3rd millenium BC Eastern Aegean has sometimes been considered a result of the exploitation of the local ore deposits (Renfrew 1969, Branigan 1971), but the case for import of metal from outside the Aegean is just as strong. The deposits most often quoted in archaeological books as the copper sources for Bronze Age Greece are those of Cyprus and Ergani Maden in Eastern Turkey. More recently, lead isotope work has proved that in fact there is not much evidence for the use of either of those ore sources in the Bronze Age Aegean (Stos-Gale and Macdonald 1991). Several Greek copper deposits have been brought to light through the lead isotope and archaeometallurgical work. Table 7 shows a compilation of information on the Mediterranean ore deposits which have been archaeometallurgically explored in recent years. The lead isotope signatures of various Mediterranean copper and lead deposits have been already discussed at length in Chapter 6. The lead isotope data for ore samples analysed at the Oxford laboratory in recent years and not previously published are listed in Appendix 2. The data for the Turkish copper ore deposits used in this work are mostly compiled from the publications of the Heidelberg/Mainz group (Wagner et al. 1989 and references within) and the Smithsonian group (Yener et al. 1990). Some geological information about the ore deposits in Greece came from Dr. S. Papastavrou of the Institute of Geological and Mineralogical Exploration in Athens (IGME) who has collaborated with us since 1986. For most of the Greek, Italian and Spanish deposits, as well as for Bulgaria, Cyprus and Timna the information comes from many publications and the fieldwork carried out in recent years for the Oxford part of the British Academy Project on trade in the Bronze Age Mediterranean.

The conclusions which can be drawn from the data accumulated in Table 7 indicate that the most likely sources for the early copper metallurgy on Crete

Table 7. Mediterranean ore deposits and the evidence of their ancient exploitation.

Country	Region	Main mineralisation	Ancient mines	Smelting remains	Reference
Bulgaria	South-East and Central	Pb-Cu-Au-Ag	Ai Bunar, Chalcolithic	Yes, many slag heaps (undated)	Chernykh 1978
Cyprus	Cyprus	Cu-Fe-S	Obliterated	Great amount of slag, earliest from 2 mill.BC	Various
Greece	Chalkidiki	Pb-Ag-Cu	Roman	Roman	Wagner et al. 1986
Greece	Crete	Fe, minor Cu, Pb	Not found	Chrysokamino, small quantity of Cu slag	(see text)
Greece	Cyclades, Anaphi	Pb	None	None	NHG & ZS-G 1981
Greece	Cyclades, Antiparos	Pb	None	None	NHG & ZS-G 1981
Greece	Cyclades, Kea	Pb	None	None	NHG & ZS-G 1981
Greece	Cyclades, Kythnos	Cu-Fe	Yes, but no date	Cu slag from 3 mil. BC (C14)	ZS-G 1989
Greece	Cyclades, Naxos	Pb	None	None	NHG & ZS-G 1981
Greece	Cyclades, Seriphos	Fe-Pb-Cu	Yes, but no date	Cu slag, 2 heaps, no date	NHG & ZS-G 1981
Greece	Cyclades, Siphnos	Ag-Pb-Au-Cu	EBA date (TL and C14)	Scattered slag	Wagner et al. 1985
Greece	Cyclades, Syros	Pb-Fe	Perhaps, but no date	None	NHG & ZSG 1981
Greece	Cyclades, Thera	Pb	None	None	Own, unpubl.
Greece	Cyclades, Tinos	Pb	None	Fe slag only	IGME, S. Papastavrou
Greece	East Sporades, Chios	Pb	None	None	IGME, S. Papastavrou
Greece	Euboea	Fe-Cu-Pb	Perhaps, but no date	Fe slag only	Own, unpubl.
Greece	Lavrio	Pb-Zn-Ag-Cu	Earliest dated 3 mill. BC	Great amount of slag, litharge from 2 mill.BC	Spitaels 1979
Greece	Macedonia	Pb	Not known	? not known	IGME, S. Papastavrou
Greece	North Aegean, Lesbos	Pb	None	None	IGME, S. Papastavrou
Greece	North Aegean, Thasos	Pb-Cu-Fe	Classical?	Many slag heaps	Pernicka et al. 1988
Greece	Othrys Mountains	Cu	Yes, but no date	Cu slag heaps dated to 8-5th c. BC (C14)	Own, unpubl.
Greece	Pangeon Mountains	Pb-Au-As-Ag	Classical?	Many slag heaps, undated	Own, unpubl.
Greece	Peloponnese	Pb-Fe-Cu	Not found	Fe slag only (Y. Bassiakos)	Own, unpubl.
Greece	Rhodope	Pb-Cu	Not found	Yes, but not dated	IGME, S. Papastavrou
Greece	Samos	Pb	Not found	None	IGME, S. Papastavrou

Table 7. continuation ...

Country	Region	Main mineralisation	Ancient mines	Smelting remains	Reference
Greece	Thessaly, Pelion	Fe-Cu	Not found	None	Own, unpubl.
Israel	Timna	Fe-Cu	Chalcolithic and later	Yes, many slag heaps BA and Roman	Rothenberg 1988
Italy	Liguria	Cu	Yes, possibly EBA	Not found	R. Maggi, Chiavari
Italy	Sardinia	Pb-Zn-Cu	Yes, not dated	Much evidence for Nuragic (1 mill. BC) metall	F. Lo Schiavo
Italy	Tuscany	Fe-Cu-Pb-Sn	Yes, not dated	Only Fe slag found, Etruscan?	Various and own
Jordan	Fenan	Fe-Cu	Chalcolithic and later	Yes, many slag heaps BA and Roman	Hauptman 1989
Serbia	Rudna Glava	Cu	Chalcolithic	?	Jovanovic et.al 1976
Spain	Cartagena	Pb-Zn-Ag	Obliterated	?	Own fieldwork
Spain	Rio Tinto	Ag-Cu	??	Yes, silver extraction	Various
Turkey	Black Sea coast	Pb-Ag-Cu	Yes	Yes, many slag heaps (undated)	Wagner et al. 1989
Turkey	South, Taurus Mountains	Pb-Cu-Sn	Yes	Yes, many slag heaps (undated)	Yener et al. 1989
Turkey	South-East, Ergani Maden	Cu	Yes	Yes, many slag heaps (undated)	Wagner et al. 1989
Turkey	Troad	Pb-Ag-Cu	Yes	Yes, many slag heaps (undated)	Wagner et al. 1989

(if not from Crete itself) would be Lavrion in Attica, Kythnos in the Cyclades, several of the Turkish ore deposits (notably Troad, deposits on the coast of the Black Sea including Kure, perhaps also Ergani Maden) and may be the Near Eastern copper mines of Feinan and Timna. All those mineral deposits are (apart from the Cycladic islands) medium to large copper deposits. There are several other localities which must be also taken into account: they are the copper occurrences in the Othrys Mountains in Central Greece, mines in the Chalkidiki area, and Kirki and Essimi in Northern Greece. Perhaps also one should check the possibility that some of the earliest metal came from the areas of the Balkans where the earliest European copper metallurgy is known from the 5th millenium BC (Chernykh 1975). The lead isotope compositions of all ore deposits listed in Table 7 are known at least in a preliminary way.

7.3. Copper mineral deposits on Crete in the archaeological literature.

Some years ago, archaeologists were greatly attracted by the idea of local, Cretan, copper sources as the base for the remarkable development of Minoan metallurgy. This idea was particularly encouraged by the survey carried out on Crete in the sixties and early seventies by the French scholar Paul Faure. Faure published several papers, in which he advocates numerous small occurrences of copper as "Les mines du Roi Minos". In his 1966 paper he lists 22 sites on Crete where copper minerals are found. Most of his arguments for these mines are rather dubious. A typical description of such occurrences is similar to the one describing a "copper mineralization" near Kritsa (Mirabello Bay): " ... At one and a half hours' walk to the WSW of Kritsa one finds a great variety of eruptive rocks, bordering the high plateau of Katharo ... In such a context the geographer Raulin is the first to have described in 1845 grains of pyrites disseminated in a Cretaceous contact deposit ... I have seen traces of nickel sulphide. For many years local prospectors have mentioned the presence of carbonates of copper to the south of Katharo. For 80 years the peasants of Selakano and of Kritsa have

sold to foreigners or sent to the Archaeological service bronze weapons and votive axes coming from an unknown site ... One can hardly doubt the existence of one or many centers for the treatment of metal between Selakano and the Katharo whilst the mountain is rich in toponyms ... describing furnaces, generally of charcoal; but everyone knows that at all times one has roasted and reduced impure minerals with this fuel ...". In his narrative Faure mentions traces of minerals (not of copper!) visible in the rock in one breath with local tales and bronze weapons found in the area, and presumed furnaces for smelting metal. There is no reason why a cache of Minoan metal artefacts should have anything to do with the presence of traces of ores, and it seems more likely that either some ancient tombs or a cave sanctuary are in the vicinity of these villages. In many other places Faure gives examples of "copper carbonates of low content" and "traces of malachite in the schist" near some Minoan ruins and implies that this association proves Minoan copper smelting from the local copper minerals.

Branigan followed that line in the early seventies, when during several seasons of archaeological survey in central-southern Crete, he found and described several other occurrences of copper (Branigan 1975, 1977). Apart from the occurrence in Chrysostomos which indeed contains malachite and azurite, other mineralisations are described as consisting of "copper minerals in schist". Even more unusual is the "Early Bronze age metal source in Crete" at Fournou Korifi, where on the top of the hill "copper-bearing pebbles" were found. It seems that some chemical analyses of these pebbles were made (there is no reference in the paper as to the method or the analyst) and " ... the analysis of two of the pebbles produced 1% and 2.2% of copper ..." (Branigan 1971, 12).

On the basis of their surveys, both Branigan and Faure concluded that there are enough copper ore deposits on Crete to satisfy Minoan demands for this metal in the Early Bronze Age.

Muhly and Rapp conducted a survey in 1974 which discounted many of

the alleged copper deposits reported by Faure (Wheeler et al. 1975). They concluded that Crete probably should not be called a major producer of copper in the Bronze Age. Becker (1976) in the course of extensive field work on Crete, conducted primarily to establish soft stone sources, demonstrated also that many alleged copper sources on Crete have been incorrectly identified. Finally, in our archives there is a letter from a Cretan commercial mining engineer M. Diallinas of Heraclion, well known to many archaeologists, written in October 1977 in reply to Noel Gale, where he comments on the ideas of Faure in following way: " The occurrences cited by our mutual friend Professor Faure refer mostly to small samples found as float. In many cases the alleged site has produced no further evidence."

7.4. Copper deposits on Crete in the geological literature.

The standard handbook of European mineral deposits (Dunning et al. 1982, p.237) includes no mention of copper ores on Crete. The only mineral deposits which seem worth mentioning in the current geological literature include gypsum and iron. The Greek geologists working on this island denied the existence of all but traces of copper ores. However, it must be admitted that there is always a certain lack of understanding amongst modern economic geologists of the relatively limited requirements of the metallurgists of five thousand years ago. The modern emphasis on the non-ferrous metallic mineral deposits of the world tends to concentrate on the deposits of Australia, Siberia, America and the Far East. Bateman (1946, 479) writes: "From early times until 1800 copper was widely produced in small quantities. From 1801 to 1810 the annual world production was only 18,200 tons, equivalent to less than one month's production of some present-day mines ... The tremendous growth in the use of copper is indicated by the fact that of the total world copper produced in the last 100 years about 80 percent was mined in the last 25 years ... Annual production normally ranges from about 2 to 2.5 million tons of metallic copper."

of the whole of the Mediterranean are quite meaningless when one thinks on such a scale. Therefore it seems that the modern geological handbooks in some cases might be somewhat misleading when it comes to the search for ancient metal sources.

7.5. Copper deposits on Crete - the Oxford survey.

It seemed that the only way to find the relevant information was a survey, perhaps aided by the Cretan geologists, but with an independent assessment of the archaeometallurgical position. In the early nineteen-eighties, together with Noel Gale, we went systematically to nearly all mineral occurrences described by Faure and Branigan to collect copper ore samples for lead isotope analyses. The field work resembled a "wild goose chase". In many cases we were not able to find any real mineralization, but only some green or bluish-green colouring of the rocks. We have collected many samples which were then analysed by XRF at Oxford, but the copper in schist never materialized. Some of the other occurrences were equally unrewarding. For example, on the Fournou Korifi site, after a whole morning of searching, we had to conclude that: " Nearly all the pebbles are of blue-grey marble, a few of quartz. Some (few) of the marble pebbles bear quite a lot of Fe ore (oxides and carbonates); none was found bearing blue azurite - indeed no certain copper found at all - some trace of quartz, which also occasionally bears Fe. The peak is indeed a conglomerate - pebbles in an earlier matrix. No reason that any part of this hill should ever have contained a concentration of copper- bearing pebbles ... Fire-burnt stones not found ... No slag, no furnace lining or crucible fragments ... " (Field Notebook, August 1983).

On the other hand, Chrysokamino, the only site with some slag discovered at the beginning of this century, by a Greek archaeologist Hadjidakkis and described by Mosso (1910) as Minoan copper smelting site, proved to be a curious place on a low cliff on the north-east coast of the island with a small scatter of

copper slag. Mosso recorded that Early and Middle Minoan pottery was found there and that there was a cave nearby thought to be an ancient copper mine. There are no geologically known copper occurrences in this part of the island, but there are many important Early Minoan archaeological sites in the vicinity (amongst others Gournia, Mochlos and Pseira), but no other archaeologist has ever found any additional proof of the Bronze Age antiquity of Chrysokamino. Branigan (1968, 50-51) even suggested that the site was the scene of metallurgical operations carried out by a 14th century AD minority group of itinerant copper smiths called the *Chalkiades*. His conclusions were based to a large degree on the analysis of slag from Chrysokamino made by a Mr. C. Sargent and giving a "reasonably high" smelting temperature of 1150^0C and a large amount of limestone in the slag. In fact the quoted temperature and presence of limestone as flux is quite normal for copper smelting in the Bronze Age (Gale et al.1985). A field trip to Chrysokamino confirmed that the site is much smaller than any of the other Greek ancient copper smelting sites. The amount of slag is rather small - the surface of covered by it measures some 30 by 8 meters and the depth cannot be much beyond 50-80 cm. On the other hand, the slag pieces are very small and much of the site slopes towards the cliffs falling down to the sea; therefore more slag might have fallen down. The tiny (nut-size) slag pieces are heavily mixed with the curious pieces of furnace lining described by Mosso. The red, coarse pottery fragments have on their edges round, finger size holes. Mosso (1910) interpreted these fragments as coming from a crucible where pieces of ore were smelted by putting them into the holes on the top and heating from a sort of portable stove below. Most metallurgists have dismissed this idea as too fanciful for serious comment. Careful examination of many pieces of this 'furnace lining' on the site proved that the holes have no traces of slag. The sections of samples of slag collected by us show a very high density of copper prills. A high amount of copper in slag is characteristic of primitive metallurgy,

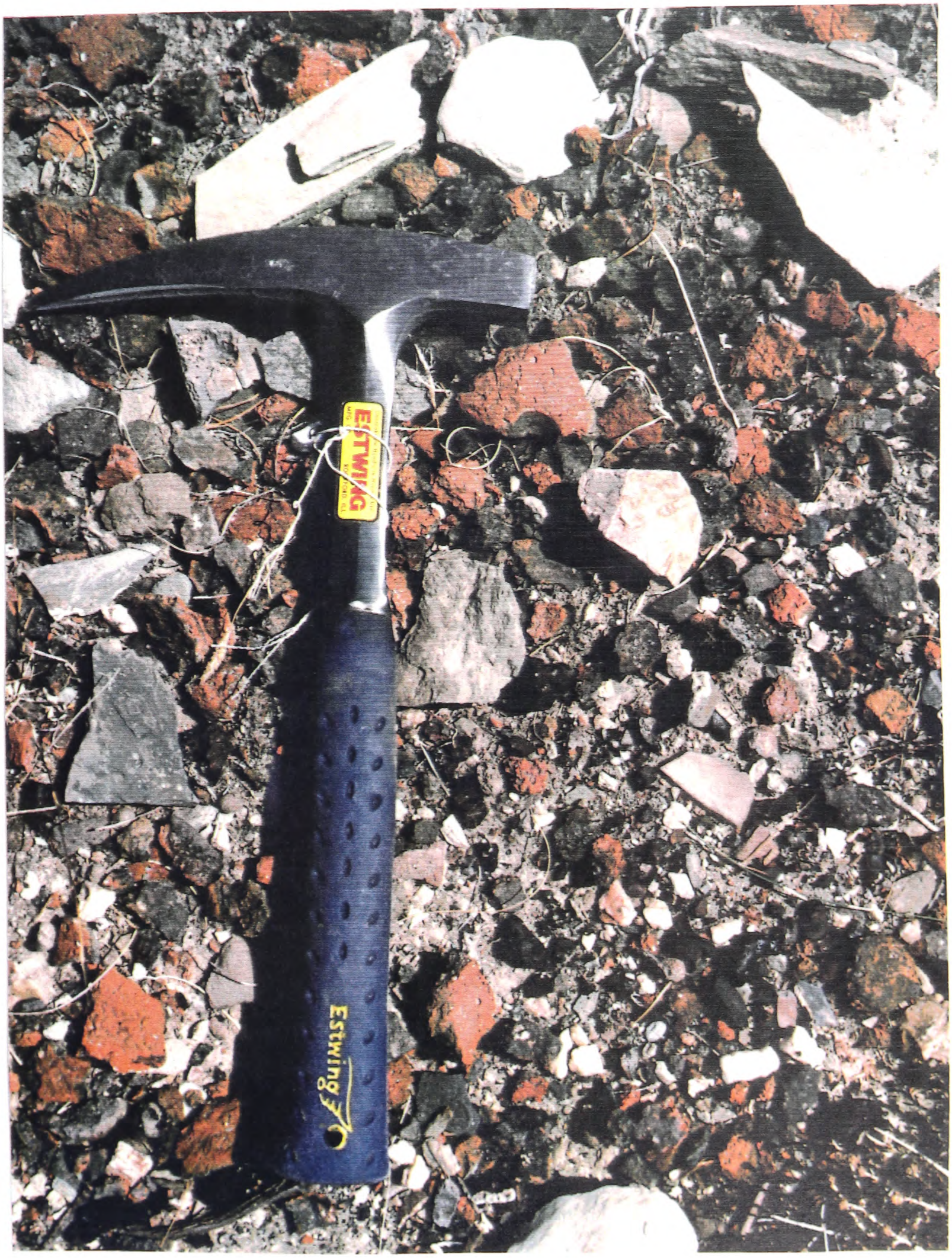
and rather unlikely for 14th century professional copper smelting. The XRF analyses of the slag show in some of the pieces several percent of arsenic. This information again points to a possibility that the slag is indeed of Bronze Age date; if the debris were from medieval copper smithing it would more likely be an alloy of copper with tin and/or zinc. Many analyses of ancient metal objects conducted in the last decades show that arsenical copper is typical only of very early metallurgy. Branigan though is quite right in saying that (Branigan 1968, p.50): "An extensive examination of this area by Dialinas produced no evidence of mineralization, a not unexpected result in this barren limestone region." In the next Chapter I will discuss the two preliminary results of lead isotope analysis of the slag from Chrysokamino. It is quite possible that the site and its surrounding area is worth much more careful examination.

Copper minerals on Crete are definitely present on two sites known to the archaeologists: one is that of Chrysostomos on the central south coast and the other is Sklavopoulou in West Crete. The latter seems most unlikely as a source of metal in the Bronze Age: the present evidence of copper mineralization consists of some green stains on the waste from a very small mining operation on the top of a high mountain (directly below the fence of a USA manned radar station). Malachite and azurite are disseminated in an iron/manganese dominated matrix. The mineralization is mainly on the surface and neither the quality or the quantity of the mineral seem to be significant even in archaeometallurgical terms.

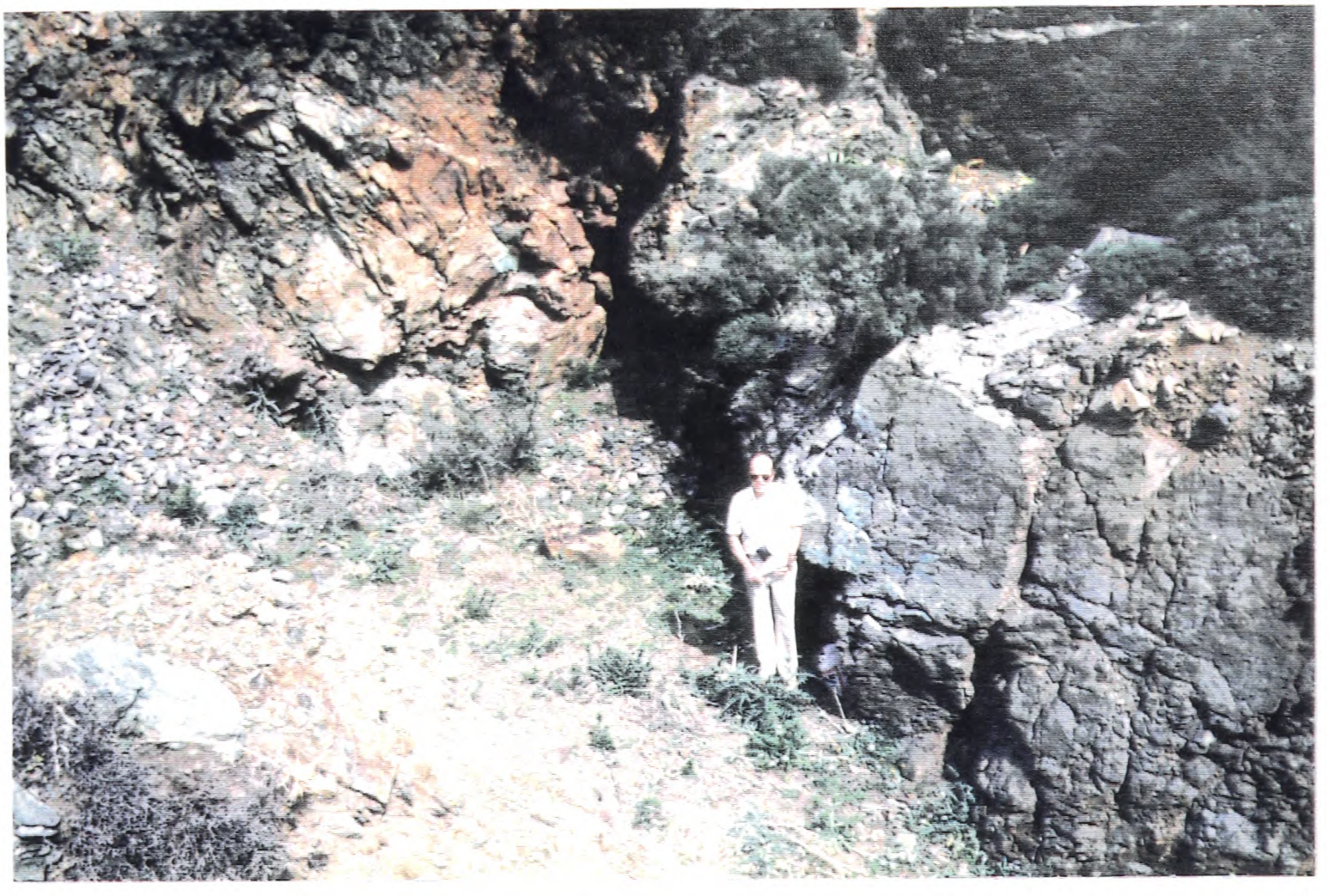
The copper mineralization on the south coast is more interesting. Branigan mentions (1968, p.51) that in the nineteen-fifties there was an attempt to mine the ore in Chrysostomos. Some malachite and azurite are still visible in the limonitic rock-cut in a large open pit. It is difficult to assess how much copper mineral there might have been present on this site some four thousand years ago. It is very unlikely that the mineralization has ever been very extensive, but some

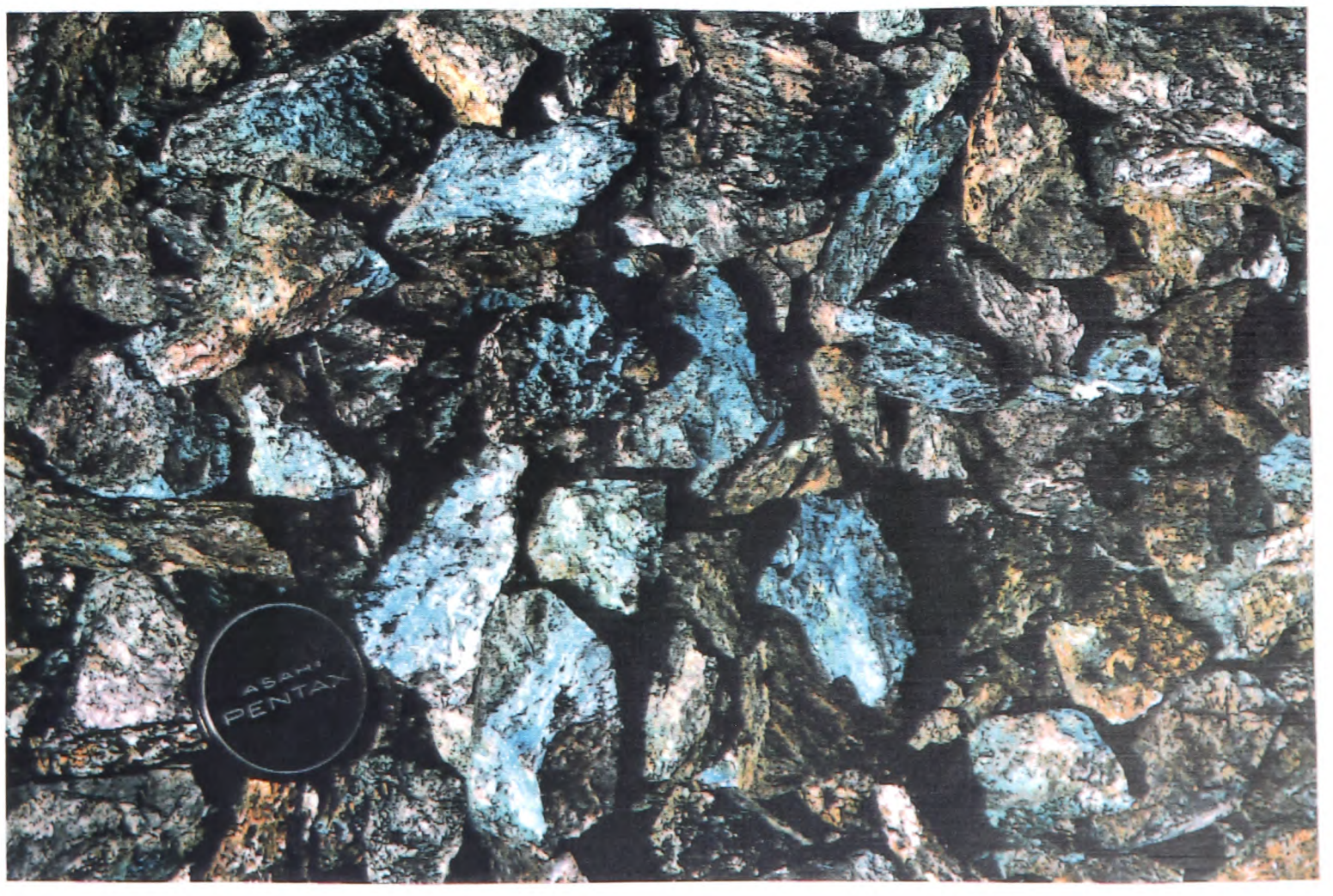
Phot. 6. The copper smelting site of Chrysokamino in the Mirabello Bay on the North-East coast of Crete.

Phot. 7. Scatter of slag and furnace lining in Chrysokamino.



Phot. 8. Surface mineralisation of copper carbonate in Chrysostomos.

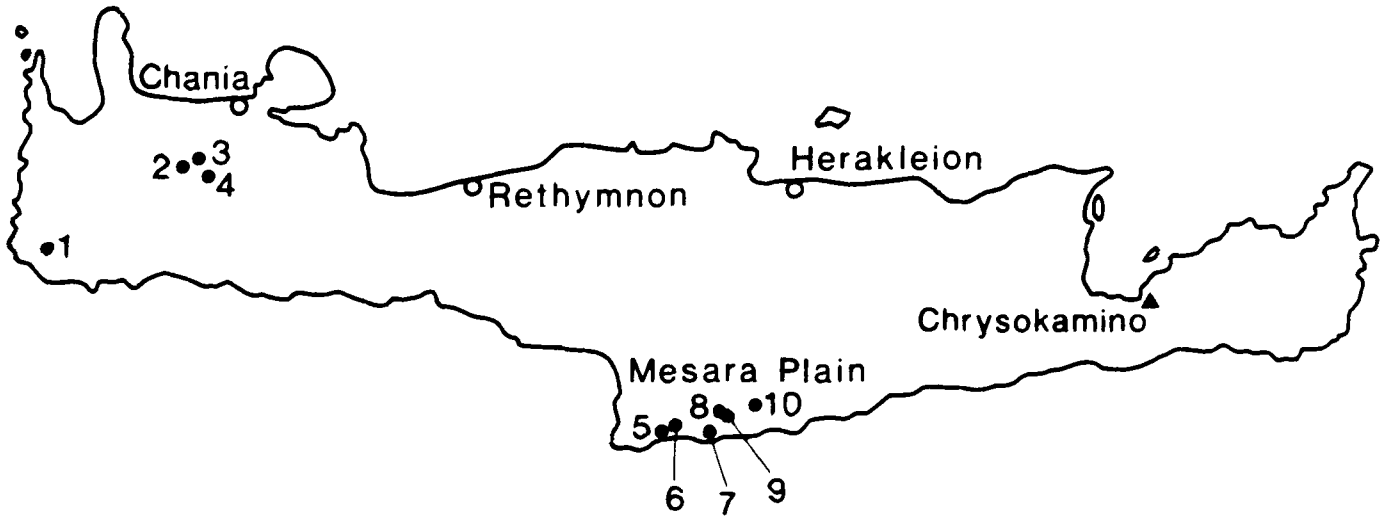




oxidised copper ores might have been visible here and might have been used to a small extent in antiquity. The occurrence is surrounded by Minoan and later sites - on one occasion the archaeologists walking with us around Chrysostomos spotted several Early Minoan shards on a field just above the pit. On the other hand there are no visible galleries or any other traces of ancient workings.

There is also one occurrence of galena in Central Crete which is sometimes mentioned in the archaeological literature. The occurrence is near the village of Ano Varsamonero and it seems that perhaps in the last century there was a small mining operation carried out there. Again, the occurrence is very small and our neutron activation analyses of samples of galena show a silver content not much above 200 ppm - a level far too low for Bronze Age silver extraction. Although Mr. Diallinas has found several other small occurrences of galena near the south coast of Crete, none of them was of any significant size (they seem to consist mostly of very small veins of galena in the rocks). When we saw him and his collection in Heraclion in 1979 he was not well enough to come with us for a field trip to show us the occurrences and his information was not very reliable. The collection of samples was rather chaotic and none of the other geologists residing on Crete confirmed any of the locations cited by Diallinas. Figure 32 shows the location of copper occurrences on Crete confirmed by the survey and suggested by Diallinas.

The results of our survey, combined with all reliable geological information about mineral deposits on Crete, indicate that significant metal extraction (copper, lead and silver) from the local ores in the Bronze Age times is very unlikely. This result leads to the conclusion that the innovative and skillful Minoan metalsmiths must have relied mainly on supplies of imported metal. The archaeological finds from Cretan sites show that Crete was in trade contact with all of the Eastern (and perhaps Western?) Mediterranean. Amongst the imported objects there are ivory, Egyptian stone vessels, scarabs and seals, many



1. Sklavopoúlou
2. Skinés
3. Fournés
4. Meskla
5. Lasaia
6. Chrysostomos
7. Lebena
8. Miamou A
9. Miamou B
10. Panagia

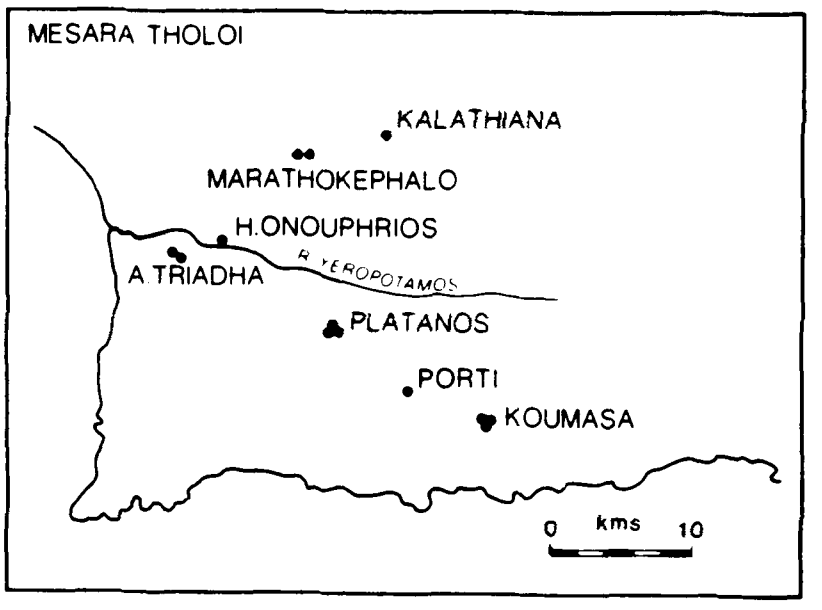


Fig. 32. Copper occurrences on Crete surveyed for the archaeometallurgical project. Sources in Western Crete do not show any traces of ancient exploitation and the type of copper mineralisation is not suitable for ancient technology. Numbers 7 to 10 in southern Crete were found by Diallinas, but not confirmed by our survey. Archaeological sites where Early Minoan weapons were found are marked in the lower part of the drawing. Chrysokamino is on the east coast of Mirabello Bay in North-Eastern Crete.

objects from the Near East and the Aegean islands and pottery from Cyprus. Throughout the Bronze Age Crete was in the centre of the trading network in the Eastern Mediterranean and supplies of metal could in principle have been coming from any part of this region. It seems that lead isotope analysis is at present the only scientific technique capable of finding out the origin of copper used on Crete for the production of the Minoan objects.

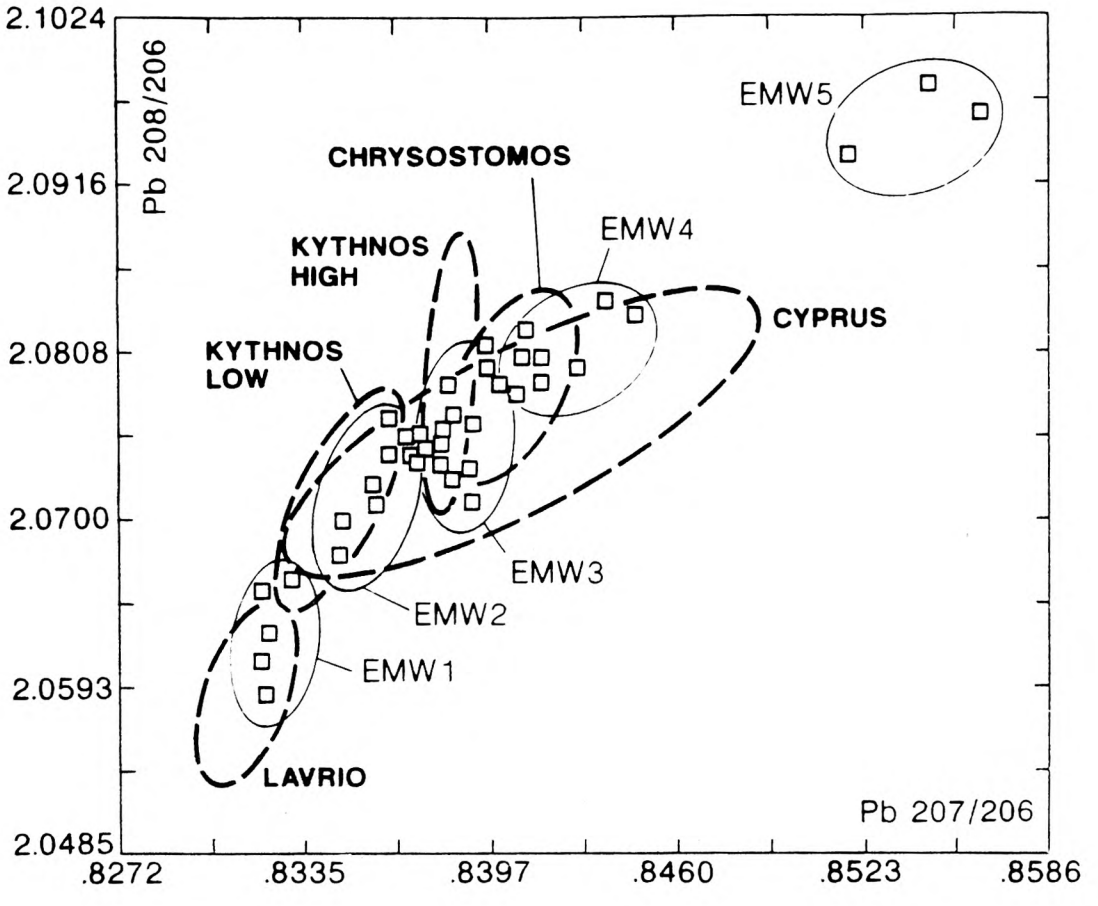
7.6. Lead isotope analyses of Early and Middle Minoan copper-based weapons.

The early Minoan Cretan weapons analysed for their lead isotope composition are listed in Table 8. The locations of the relevant archaeological sites (tholos tombs in the Mesara) are indicated on Figure 32. The metal of the weapons can be classified as arsenical copper with only a small amount of lead (in most cases below 1%); only a few of them contain tin (Junghans et al. 1974). Alloys of such composition are common in the earlier periods of the Bronze Age. Apart from tin, all other elements of the alloy are from smelting of multimetallic ores, rather than deliberate alloying of different metals (for discussion see Chapter 5). Figure 33 represents the bivariate plot of the lead isotope analyses of early Minoan weapons analysed for this study. For comparison, there are also included on this diagram the ellipses showing the extent of the lead isotope fingerprints of copper ore deposits falling in this region of the lead isotope diagram. The ellipses have been calculated for a number of ore samples analysed in our laboratory. A number of copper deposits mentioned earlier can be instantly rejected as inconsistent with the lead isotope fingerprints of these weapons. In this category are the important deposits in the Balkans and Northern Greece, Sklavopoulou, Ermioni and Ergani Maden. It is also clear that the probability of Cypriot copper being used for these weapons is very low.

The comparatively large range of the lead isotope ratios measured for the early Minoan weapons indicates that the artefacts do not originate from a single

ore deposit. The theory of the development of lead isotope composition and the experimental data presented in Chapters 4, 5 and 6 provide the evidence that the range of lead isotope compositions of ores in one uniform geological formation usually can be expected not to exceed 0.5%. The Cypriot lead isotope fingerprint, which on Figure 33 covers a wider range, represents a cluster of several different fingerprints of ores from various copper deposits on Cyprus (see Chapter 6). The lead isotope composition of the majority of the Early Minoan weapons is concentrated around the values of 2.0754, .84 and 18.7. These lead isotope compositions fall on the edges of three isotopic fingerprints of ores: Kythnos High, Chrysostomos and Cyprus. On the upper (208/206 versus 207/206) diagram of Figure 33 it seems equally likely that the metal used for those weapons originated from any of these three copper deposits. However, the second plot (206/204 versus 207/206) shows the majority of the artefacts now falling above the Chrysostomos and Cyprus fields. Apart from this major central group of weapons, two other isotopic groups of objects can be distinguished on this diagram: two axes from Ayia Photia (4660 and 4667), a bronze adze (1533) and a triangular dagger (1265) from Ayia Triadha plus an undated dagger from Mochlos (1556) form a group (EMW1) which seems to be consistent with the fingerprint of the Lavrion ores, and two triangular daggers (1280 and 1285) and a long dagger (1295) from Ayia Triadha plot far away in the much higher 208/206 region of the diagram (EMW5).

Sorting out the lead isotope data in the order of magnitude, one can see that the data in the large central group divides into three smaller groups (marked EMW2, EMW3 and EMW4). The division into these groups was adjusted using discriminant analysis. The isotope group numbers allocated to each weapon are listed in Table 8 and the print-out of the probabilities of each object belonging to the allocated EMW group is enclosed in Appendix 3;A. The discriminant calculations performed by the BMDP 7m show that posterior probabilities of



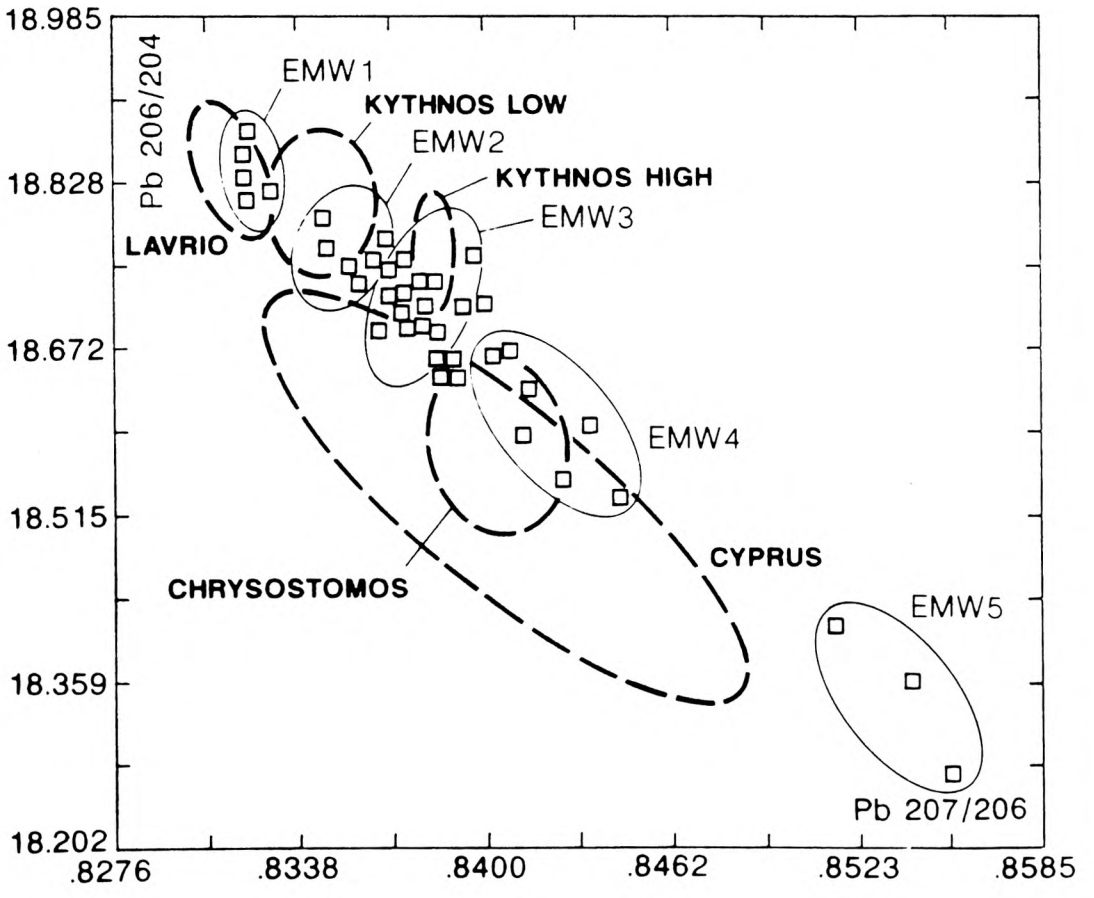


Fig. 33. Bivariate plot of the lead isotope ratios measured for the early Minoan weapons and matching copper ores.

each of the objects belonging to the selected group are very high (in all but two cases over 70%). Only two objects from group EMW3 (cases 12 and 13, which correspond to daggers 1278 from Ayia Triadha and 1878 from Platanos) should be perhaps re-located to EMW2. The lead isotope measurements of the object No. 1876 were rather poor, so the data might in fact have a higher analytical error than the other objects belonging to this group. Similarly, object No. 1871, another dagger from Platanos, did not run very well and is being left out altogether from the further discussion.

The next step is the comparison of the isotope groups formed by these objects to the relevant groups of lead isotope compositions of the ore deposits. Groups EMW2 and EMW3 correspond best to the two Kythnian isotope fields, and group EMW4 seems to be on the edges of the ores from Chrysostomos and from Cyprus. The nearest lead isotope ratios of copper ore deposits corresponding to EMW5 are found amongst the lead isotope data of the ores and slags from the Turkish Black Sea coast at Kure and the ores from the Othrys Mountains in Central Greece. The numerical probabilities of the origin of each weapon from these ores were calculated using linear stepwise discriminant analysis (BMDP 7m). Statistical comparisons of the lead isotope ratios of the objects and the ore data using the stepwise discriminant analysis are printed in Appendix 3;B. The column 'BMDP No.' in Table 8 lists numbers used by the software corresponding to the museum numbers of the object; in this way each artefact can be readily identified in the statistical tables in Appendix 3;B and its origin from a given ore deposit is given numerical probability.

7.7. The origin of metal used for the weapons and the copper production in the Early Bronze Age Aegean.

In the first isotopic group of the Early Minoan weapons three of them have high probabilities of originating from the Lavrion minerals. They are: bronze double adze from Ayia Triadha No. 1533 (50.4% probability), a dagger from

Table 8. Lead isotope data and origin of metal of the early Minoan weapons.

BMDP No.	Object number	Chronology	Site	Description	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb	Isotope group	Origin
58	9943	EMI-LM	Aghios Onufrios	Dagger	2.07555	.83737	18.758	EMW3	Kythnos high
47	4670	EM II	Ay. Photia	Dagger	2.06771	.83464	18.799	EMW2	Kythnos low
49	4675	EM II	Ay. Photia	Axe/adze	2.07242	.83570	18.749	EMW2	Kythnos low
52	4657	EM II	Ay. Photia	Axe/adze	2.07446	.83637	18.759	EMW2	Kythnos low
55	4672	EM II	Ay. Photia	Dagger, killed	2.07368	.83695	18.755	EMW3	Kythnos high
68	4658	EM II	Ay. Photia	Dagger with cloth	2.07122	.83899	18.661	EMW3	Kythnos/Cyprus?
114	4660	EM II	Ay. Photia	Axe/adze	2.06278	.83217	18.878	EMW1	Lavrio
115	4667	EM II	Ay. Photia	Axe/adze, small	2.06624	.83295	18.822	EMW1	Kythnos low
21	1280	EMI-MMIa	Ayia Triada	Triangular dagger	2.09368	.85170	18.411	EMW5	Kure/Othrys?
22	1295	EMI-MMIa	Ayia Triada	Long dagger	2.09794	.85431	18.359	EMW5	Kure/Othrys?
23	1285	EMI-MMIa	Ayia Triada	Triangular dagger	2.09631	.85595	18.268	EMW5	Kure/Othrys?
47	1263	EMI-MMIa	Ayia Triada	Triangular dagger	2.07801	.84046	18.671	EMW4	Chrysostomos
48	1264	EMI-MMIa	Ayia Triada	Triangular dagger	2.08216	.84084	18.675	EMW4	Chrysostomos
49	1277	EMI-MMIa	Ayia Triada	Triangular dagger, type I	2.08043	.84097	18.512	EMW4	Chrysostomos/Cyprus
50	1272	EMI-MMIa	Ayia Triada	Triangular dagger	2.08066	.84098	18.676	EMW4	Chrysostomos
50	727	EMI-MMIa	Ayia Triada	Dagger	2.07127	.83592	18.735	EMW2	Kythnos low
51	1258	EMI-MMIa	Ayia Triada	Triangular dagger	2.07899	.84137	18.634	EMW4	Chrysostomos
53	1278	EMI-MMIa	Ayia Triada	Triangular dagger	2.07543	.83679	18.778	EMW3	Kythnos high
55	1292	EMI-MMIa	Ayia Triada	Long dagger	2.08410	.84347	18.599	EMW4	Chrysostomos
57	1291	EMI-MMIa	Ayia Triada	Triangular dagger type IV	2.07541	.83732	18.725	EMW3	Kythnos high
60	1269	EMI-MMIa	Ayia Triada	Triangular dagger type I	2.07463	.83762	18.695	EMW3	Kythnos high
61	1268	EMI-MMIa	Ayia Triada	Triangular dagger, type I	2.07487	.83786	18.693	EMW3	Kythnos high
63	1271	EMI-MMIa	Ayia Triada	Triangular dagger	2.07387	.83811	18.709	EMW3	Kythnos high
64	1281	EMI-MMIa	Ayia Triada	Triangular dagger	2.07912	.83825	18.737	EMW3	Kythnos high
72	1532	EMI-MMIa	Ayia Triada	Double axe	2.07866	.83997	18.720	EMW3	Kythnos high

Table 8. continuation ...

BMDP No.	Object number	Chronology	Site	Description	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb	Isotope group	Origin
111	1265	EMI-MMIa	Ayia Triada	Triangular dagger	2.06600	.83203	18.857	EMW1	Kythnos low
112	1533	EMI-MMIa	Ayia Triada	Double adze	2.06096	.83205	18.836	EMW1	Lavrio
56	1495	EMI-MMIa	Kalathiana	Triangular dagger type I	2.07510	.83730	18.707	EMW3	Kythnos high
48	9423 ??	EMIIa-MMIa	Koumasa	Dagger	2.07006	.83476	18.767	EMW2	Kythnos low
52	1181	EMIIa-MMIa	Koumasa	Long dagger, type IIIa	2.08064	.84143	18.593	EMW4	Chrysostomos
66	M16	EMIIa-MMIa	Malia	Dagger	2.07305	.83858	18.664	EMW3	Kythnos/Cyprus?
56	2008	EMII-MMIa	Marathokephalo	Triangular dagger, type I	2.08369	.84473	18.537	EMW4	Chrysostomos
65	2006	EMII-MMIa	Marathokephalo	Triangular dagger type II	2.07684	.83843	18.689	EMW3	Kythnos high
69	2011	EMII-MMIa	Marathokephalo	Spearhead with tang	2.07622	.83919	18.648	EMW3	Kythnos high
113	1556	EM/LM	Mochlos	Dagger	2.05892	.83206	18.812	EMW1	Lavrio
51	1359	EM/LM	Palaikastro	Long dagger	2.07993	.84257	18.550	EMW4	Chrysostomos/Cyprus
	1871	EMIII-MMII	Platanos	Dagger	2.07495	.83317	18.920		Kythnos?
53	1877	EMII-MMI	Platanos	Long dagger, type IVa	2.09342	.84203	18.743	EMW4	Chrysostomos?
54	1876	EMII-MMI	Platanos	Long dagger typeIV	2.07383	.83682	18.725	EMW3	Kythnos high
59	1860	EMII-MMI	Platanos	Long dagger, type 5a	2.07517	.83740	18.714	EMW3	Kythnos high
62	1931	EMII-MMI	Platanos	Long dagger, type IV	2.07587	.83806	18.736	EMW3	Kythnos high
67	1934	EMII-MMI	Platanos	Dagger	2.07337	.83886	18.646	EMW3	Kythnos/Cyprus?
70	1881	EMII-MMI	Platanos	Dagger	2.07983	.83946	18.713	EMW3	Kythnos high
71	1842	EMII-MMI	Platanos	Triangular dagger, type I	2.08128	.83965	18.764	EMW3	Kythnos high
51	1927.1260	EM	Psychro Cave	Votive axe/adze	2.07658	.83631	18.691	EMW2	Kythnos low

Mochlos No. 1556 (80.9%) - this object might be in fact of a later date - and an axe-adze from Ayia Photia No. 4660 (22.1%). The other two weapons from this group - a triangular dagger from Ayia Triadha No. 1265 and a small axe-adze from Ayia Photia No.4667 show higher probabilities (16.6% and 22.1% respectively) of belonging to the group of ores and slags designated Kythnos Low, rather than to Lavrion (2.4% and 1.9%). The origin of copper metal from the Lavrion deposit in Attica does not come as a surprise. This source of metal seems to have been of importance to the Aegean world throughout Antiquity. Silver, lead and copper were smelted there in different periods of prehistory in varying quantities. What **might be** surprising is the great rarity of this metal amongst the Early Minoan weapons. As has been mentioned earlier, the dagger from Mochlos is made of tin bronze and could be of a Late Bronze Age date; the same is true for the double adze from Ayia Triadha. The small axe-adze from Ayia Photia has a lead isotope composition falling between the Lavrion and Kythnos Low field, so in fact might not be from Lavrion, but from Kythnos, the case strengthened somehow by the fact that all other objects from Ayia Photia are consistent with the Kythnian fields.

The second and third isotopic groups plot side by side and the objects falling on the touching edges of the two are obviously 'border cases' which can belong to either of the groups. In fact, both reference groups, Kythnos Low and Kythnos High, were constructed largely from the lead isotope data obtained from the same third millenium copper slag heap called Skouries from the Cycladic island of Kythnos (Stos-Gale 1989). However, all copper ores from the occurrences on the island of Kythnos plot only in the Kythnos Low field. The only ores which are consistent with the Kythnos High field (as outlined by a group of copper slags from Skouries) are the samples of minerals from Siphnos (Gale and Stos-Gale 1981). On the other hand, several samples of copper slags from two undated ancient copper slag heaps on the island of Seriphos fall

squarely into the Kythnos low field. It must be mentioned here that the island of Siphnos is mostly known for its silver and lead production in the Early Bronze Age (Gale and Stos-Gale 1981, Wagner et al. 1988), but some copper ores have been also found there (Pernicka 1988, 668, Table 13). Pernicka also found a piece of a copper slag near the mines of Ayios Sostis on Siphnos and suggested that: "...a contemporary smelting of copper and silver containing lead is possible ... but since the copper slag is relatively rare, the copper smelting must have played a small role only in comparison with smelting of lead and silver." (op.cit. p.675) It seems that copper slag of an Early Bronze Age date and consistent with the lead isotope composition of the Siphnian ores is **very** common on the next Cycladic island - Kythnos. The island of Seriphos does not have any large copper occurrences and during our geological field survey in 1982 we were able to find only a few copper minerals (chrysocolla, a copper silicate) in Koundouro (Phot. 9). The galena occurrences are in a quite different part of the island and their lead isotope compositions (Gale and Stos-Gale 1981) are quite different from any of the Kythnian and Siphnian ores and slags. To solve this puzzle, it seems quite important that more lead isotope analyses of **copper ores** from Seriphos, Siphnos and, if possible, from other Cycladic islands are made. None of these islands has any large copper occurrences and finding the right minerals might take some time. The two large ancient copper slag heaps of Kephala and Avyssalos on Seriphos were quite a surprise to the IGME geologists, who thought it impossible that enough copper ore was ever found on Seriphos itself to support this extensive copper production (Dr. S. Papastavrou, private communication). Some amount of copper slag was found also by Greek archaeologists on the island of Kea (Caskey et al. 1988). We have in our collection two single samples of disseminated copper ore from Kea and Mykonos given to us in Athens by V. Avdis (formerly of IGME), but as yet we ourselves have not able to find any more of copper ores on these islands and Dr.

Papastavrou has no knowledge of any such occurrences.

Two samples of slags from the site of Chrysokamino on the northern coast of Crete show lead isotope compositions consistent with the objects in groups EMW1 and EMW3. At present, this data can be treated only in a preliminary way, because there is no reliable dating of this smelting operation and the similarity of the lead isotope compositions might be irrelevant if these slags are of a later date. More fieldwork and many more lead isotope and chemical analyses are needed to establish the real character of the Chrysokamino site. Some means of scientific dating of the smelting operations might be possible (C-14 or thermoluminescence, perhaps). It may be that, after all, there is somewhere in the vicinity of this site a small copper occurrence. It cannot be excluded however, that there was Early Bronze Age copper smelting on this site and that the ore for metal extraction was brought here from other occurrences in the Aegean. About a mile north from Chrysokamino, beyond high cliffs, there is a quiet sandy bay ideal for beaching small boats. Perhaps the Minoan copper was obtained by bringing together ores from several coastal localities in the southern Aegean to a few, possibly secret, selected smelting sites.

Nevertheless, it is clear already that in the Early Bronze Age, certainly on Kythnos, and perhaps on Siphnos, Seriphos and Kea, there was quite a considerable production of copper metal. Kythnos might have had more suitable copper minerals than Seriphos, but the lead isotope compositions of the slags from Skouries on Kythnos indicates that the site might have been used for smelting copper minerals brought there as well from other Cycladic islands. One must remember that smelting of copper metal from its ores is a highly skilled operation. Any large scale copper production, and the amount of slag on Kythnos is quite substantial, must have been carried out by a specialised group of metallurgists who were prospecting for suitable ore sources and then smelting the metal. It is very unlikely that such technically skilled tasks could have been

Phot. 9. Copper minerals found in Koundouro on the island of Seriphos.

Phot. 10. Ancient copper slag on Seriphos.

carried out by amateurs. Smelting of the ore requires special conditions: good supplies of wood, strong winds or the means of producing forced draughts, and finally the minerals used as ores and fluxes are the essential ingredients of metal smelting. The Cycladic islands have plenty of wind! Water and flux (silicates and calcite) are also easily available. At present, most of the Cycladic islands have very few trees, but it is not impossible that the conditions in the third millenium BC were different in this respect - perhaps, even, metallurgy may have contributed to the deforestation of these islands. One can imagine that once a good smelting site was found it might have been more convenient to ship from time to time some quantity of ore into the same place where the smelting was carried on. This approach is known from the past century in many smelters in Greece and also from the large ancient copper production site in Feinan, Jordan (A. Hauptman, lecture given in the Institute of Archaeology, London, October 1992). The remoteness of the Kythnos slag heap - it is situated on a high cliff and the nearest landing bay (Ayios Yoannis) is an hour's walk away - might have been an advantage if the operation was to be kept secret and safe. The other Aegean copper smelting sites mentioned in this chapter have strikingly similar locations.

The question which now comes to mind is: how unique are the lead isotope compositions of Chrysostomos and 'Kythnos'? Our quite comprehensive Eastern Mediterranean lead isotope data base does not show any significant overlap of other copper ores with the Kythnian fields. There are, however, several copper deposits in north-west Turkey published by the German team which seem to have lead isotope compositions falling at least partly in this region of the diagram. The copper occurrences surveyed by Wagner et al. (Seeliger et al. 1985) in the Troad peninsula have been already discussed in Chapter 6. Figure 34 shows again the lead isotope data published for N-W Turkey and our lead isotope ratios for the slags and ores from Kythnos. It was pointed out already

in Chapter 6 that from single analyses it is impossible to judge the degree of isotopic similarity between the mineralizations in these two distinctly different geographical regions, but the coincidence of presently available lead isotope data must be reported.

Figure 34 also shows the lead isotope compositions of weapons from Ayia Triadha compared with the Aegean copper ore lead isotope fields and the single published analyses of the North Anatolian copper ores. The points numbered 133, 142, 143, 156 and 192 represent single sample analyses of copper ores from north-west Turkey which are listed as 'TG' numbers in Table 7. Without more lead isotope measurements of the copper ores from these Turkish deposits it is very difficult to assess the degree of the overlap between them and the Aegean ore deposits. However, at present one has to keep in mind the possibility that the signature described in this study as Kythnos Low might overlap to an unknown degree with the signatures of some of the copper ores from the North-West Turkey. Two points marked 188 are of the only so far published samples from the mines of Ikiztepe near the Turkish/Bulgarian border and they fall near the ores from Chrysostomos and Cyprus. None of the published lead isotope data for Turkish ores overlaps with the greatest concentration of the lead isotope compositions of the weapons (lower part of the Kythnos High field). In the light of the archaeological and C-14 dating of the copper slags on Kythnos which agree well and prove Early Bronze Age copper smelting on the site of Skouries (Stos-Gale 1989) it seems quite reasonable to accept at present that the two isotope groups of Minoan weapons described in this study (EMW2 and EMW3) are the result of Cycladic metal production. It seems certain that in due course there will be more published lead isotope analyses of copper ores from Turkey (two archaeological/archaeometallurgical groups are at present working there) and then the data should be again reassessed.

Appendix 3;B lists the statistical evaluation of the probability of each of

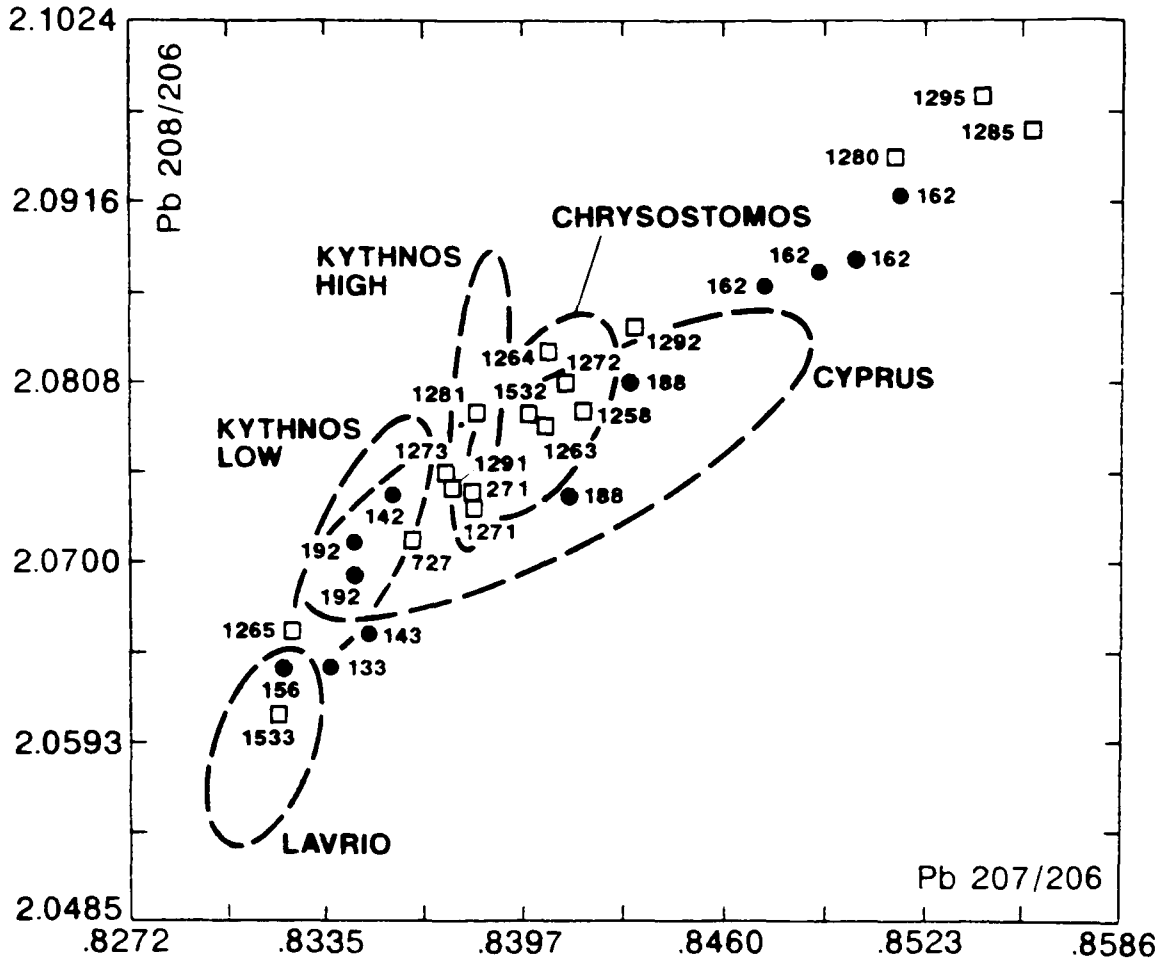


Fig. 34. Lead isotope compositions of early Minoan Cretan weapons (open squares), the Aegean ore deposits (ellipses) and single analyses of Turkish copper ores (black circles).

the objects belonging to one of the Kythnian fields. The probabilities of EMW2 belonging to Kythnos Low are between 16 and 50 percent, with two samples having nearly equal probabilities of belonging to either of the Kythnian groups. The range of the probabilities of EMW3 belonging to Kythnos High are between 10 and 79 percent with three samples forming a core of EMW3 group (66-68) showing very low probability (0.5 to 3 percent) of their association with Kythnos High. These three samples have lead isotope compositions falling in between the two Kythnos groups and might be a typical example of mixing of metal from both groups. Since both reference groups are based on analyses of ores and slags from the Cycladic islands, and, more specifically, the metal falling into these groups is consistent with its origin from the copper smelting site on Kythnos, the archaeological conclusions are not affected by the low probabilities of origin. At present there is no other ore which shows a lead isotope composition closer to the Minoan weapons than the Cycladic ores and slags. Many more analyses of slags from Kythnos are needed to confirm that indeed there is a significant division of their lead isotope compositions. It may be that more systematic analyses of slags from different parts of the slag heap can define areas where different ores were smelted. On the other hand, more analyses might prove that the division is only superficial and that in fact all slags fall together in one large group; then the three weapons falling in the middle between the Kythnian fields would have reference slag samples matching them more closely. More lead isotope analyses of copper ores from Cycladic islands should confirm or disprove the theory that the smelting of ores of various origin was performed on this island.

It is also quite likely that there has been a certain amount of mixing of the metal of slightly different lead isotope composition during the production of the weapons. The comparatively small scatter of lead isotope data of the artefacts does not indicate, however, that there was much mixing of metal from distant

and isotopically very different sources. Figure 33 shows clearly that the majority of metal is characterized by a very limited range of lead isotope compositions.

The two remaining lead isotope groups (EMW4 and EMW5) are quite distinct and not very numerous. Group EMW4 includes 10 weapons from different sites. Their lead isotope composition is closest to the few lead isotope analyses of the copper ores from the Chrysostomos copper mineralization in southern Crete. They also plot on the edge of the Cypriot ore field, but for each of the weapons the probability of any of those objects being made from Cypriot copper is lower than in comparison to the Chrysostomos ore (group EMW4, Appendix 3;B). This conclusion might be a little surprising in view of large number of Early and Middle Cypriot copper artefacts found on Cyprus. On the other hand, the archaeological evidence for **smelting** of copper on Cyprus in these periods is rather limited. The excavated smelting remains indicate that the production of copper on Cyprus was not very extensive until the middle part of the Aegean Late Bronze Age (13th to 12th century BC). The Chrysostomos copper ores remaining on this site are of the type which was certainly used in the early phases of metallurgy (carbonates). Smelting of some copper from this small mineralization of the central-southern Crete in the Early Bronze Age is quite possible. There is no direct evidence at present of copper smelting in that part of Crete, but the whole of the Mesara Plain and the coast is densely populated and of high agricultural importance. In such areas, any small traces of copper extraction, similar in size to Chrysokamino for example, would have been easily obliterated in past centuries. However, Diallinas mentioned to me that some "slag" was found on the beach at Lebena, some 20 kilometers east from Chrysostomos. Our search for slag along the Cretan beaches did not bring any finds, but it must be said that copper carbonates are still visible in Chrysostomos, and the site is surrounded by Early Minoan sites. The limited number of objects consistent with the lead isotope composition of ores from Chrysostomos

might be accidental (more analyses might show more metal of this composition), or perhaps indeed the 'Cycladic' metal production was more competitive on the Early Minoan metal market.

There is also another alternative to the origin of these objects which fall into the Chrysostomos lead isotope field: such lead isotope compositions might result from a melting together of metal, for example from Kure and the Cyclades. If indeed there was a certain amount of northern Anatolian metal in circulation in the Aegean, depending of the lead content of such scrap, it might or might not show in the lead isotope composition of the objects made from such a mixture. Any further discussion of the origin of these objects must be based on chemical analyses of various ores and objects, as well as many more lead isotope data from Turkish ore deposits.

The three daggers from Ayia Triadha forming the EMW5 lead isotope group are at present of rather mysterious origin. Isotopically closest to those daggers are samples from the ore deposits of Kure (Turkish coast of the Black Sea) and Othrys (Mainland Greece, 200 km north of Athens). However, the number of ore analyses from these two deposits is very limited at present and statistical comparison of the available data does not show a very high probability that these ores and the three daggers from Ayia Triada are of the same origin (group EMW5 in Appendix 3;B). In this particular case, metal from the Black Sea coast seems a more probable solution. Our survey of copper ore occurrences in the Othrys mountains indicated that the exploitation of this resource might have been quite important in the later periods. We collected some samples of charcoal from copper slags which were dated in the Oxford Radiocarbon Unit to 9th to 4th century BC. So far, there is no definite evidence of any earlier metal production in this area. However, only much more extensive study of the Othrys slag heaps combined with archaeological excavations can provide a more definite answer. On the other hand, we have records of many other Bronze Age objects

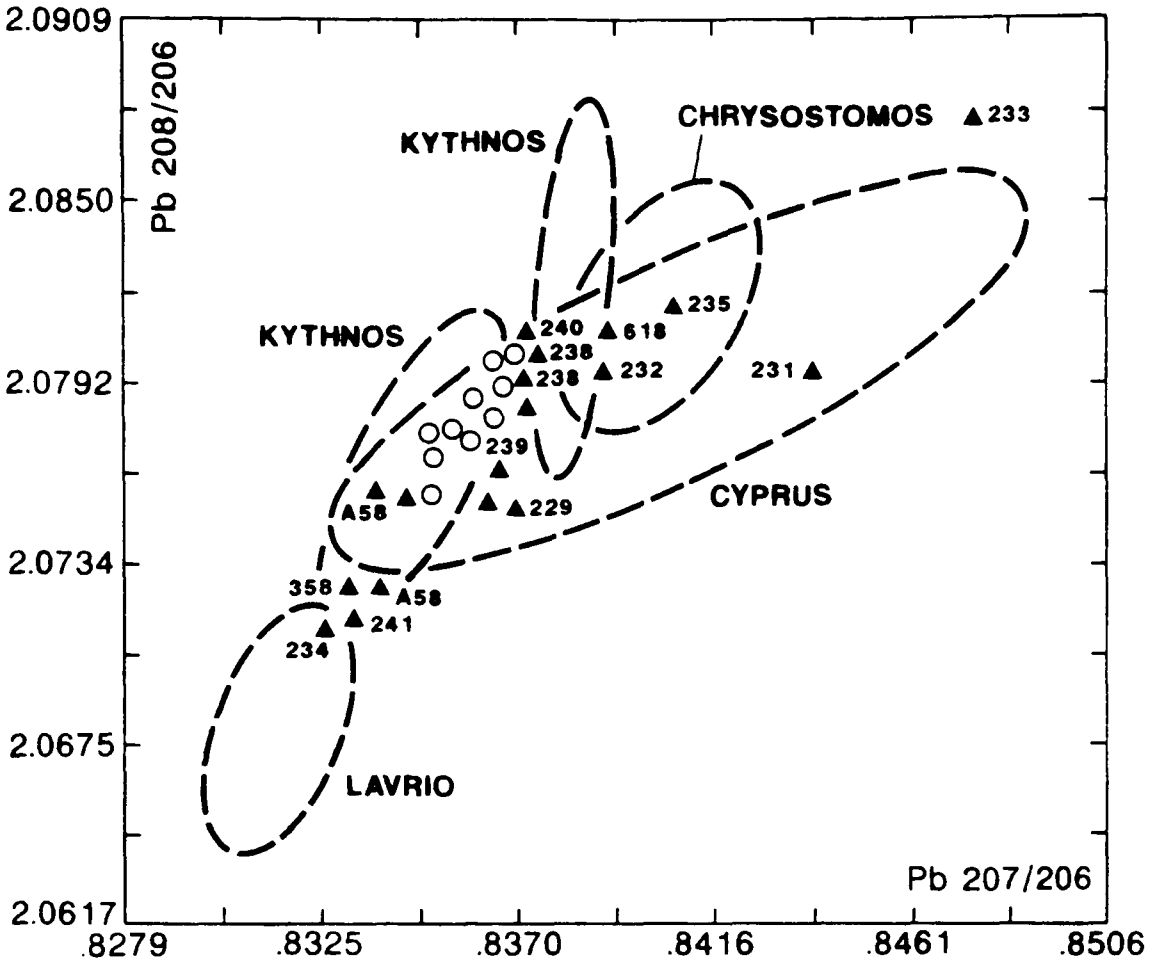
from Greece which fall into the same region of the lead isotope diagram, and more convincingly with the Turkish ores. This problem will soon be discussed in another publication, with, one hopes, more ore data for comparison from the Mainz and Smithsonian groups. However, even with the limited amount of data available at present, it seems that a certain amount of copper metal was coming to the Aegean in the Early Bronze Age from the direction of the Black Sea (Stos-Gale 1992).

Perhaps we should examine now also Renfrew's remark mentioned at the beginning of this chapter, that the first daggers seem to appear simultaneously in the Aegean in Troy I period in Troy, Thermi and Poliochni. As yet, there are no lead isotope analyses of weapons of this period from the first two sites, but Pernicka (et al. 1990) published analyses of two axes and three daggers from Poliochni which are contemporary to Troy I-II. Both axes (No. 876 and 878, from Poliochni Red period) are consistent with an origin from Kythnos Low and Kythnos High respectively. The lead isotope ratios of 878 fall amongst the Kythnos hoard artefacts, and 876 is firmly placed in the middle of the highest concentration of the Early Minoan weapons (group EMW3 consistent with Kythnos High). The three daggers from the Poliochni Yellow period plot respectively with the EMW4 (907 and 908), and EMW5 (936). This result is most exciting. Does it really mean that the Aegean metallurgy developed in the north-east and then spread south to Crete? On the other hand, could it all have started in the Cyclades, where the metals were smelted by professionals, and radiated in all directions? At present there are altogether more than 200 lead isotope analyses of copper artefacts from the EBA north-east Aegean (Pernicka et al. 1984, Stos-Gale and Gale 1984, Pernicka et al. 1990, Stos-Gale 1992a). It is quite clear that metals from Troy and Poliochni show a much greater variety of origin of metal sources, than do the Cretan and Cycladic artefacts. The majority of the earliest small pins and punches from Thermi is not identical in their

origin with the Cretan weapons, but also might have been made from Cycladic copper (Stos-Gale 1992a). The large number of isotopic analyses of metals from Poliochni (Pernicka et al. 1990) show that on this site many more sources of copper were used, and some of them are definitely from Mainland Turkey, but some are from the Aegean (lead and silver from Lavrion and Siphnos, for example). Generally, it seems that whilst the majority of metal finds from the central and southern Aegean is consistent with their origin from Cycladic copper minerals, the proportion of Anatolian metal in the Troy-Thermi-Poliochni groups is larger. However, there is still a great need for much more archaeological and scientific work in this area to clarify the picture.

7.8. The origin of weapons from the Cycladic islands and Cyprus from the period contemporary to the Early Minoan times.

The lead isotope analyses show that the majority of the Early Minoan weapons was most likely made from copper imported to Crete from the Cycladic smelters. If indeed the Cycladic islands were so prolific in their copper production, then the weapons made and found on these islands should certainly reflect the local copper smelting industry. Some time ago, a number of Cycladic daggers, axes and spearheads from the collections of the Ashmolean and the British Museums was analysed at Oxford for their lead isotope composition (Gale and Stos-Gale 1989 and Stos-Gale 1989). Figure 35 shows these lead isotope data in exactly the same lay-out as previously plotted for the Early Minoan weapons (see Figure 33). It is quite clear that the pattern of the lead isotope compositions of these two groups is remarkably similar: the majority of lead isotope ratios falls into the Kythnian fields, while some objects seem to be consistent with the Cyprus/Chrysostomos lead isotope region. Two spearheads from the Ashmolean (AE 231 and AE 233) stand out from the main group and might be made of metal originating either in Cyprus or, more likely, in north-west Anatolia.



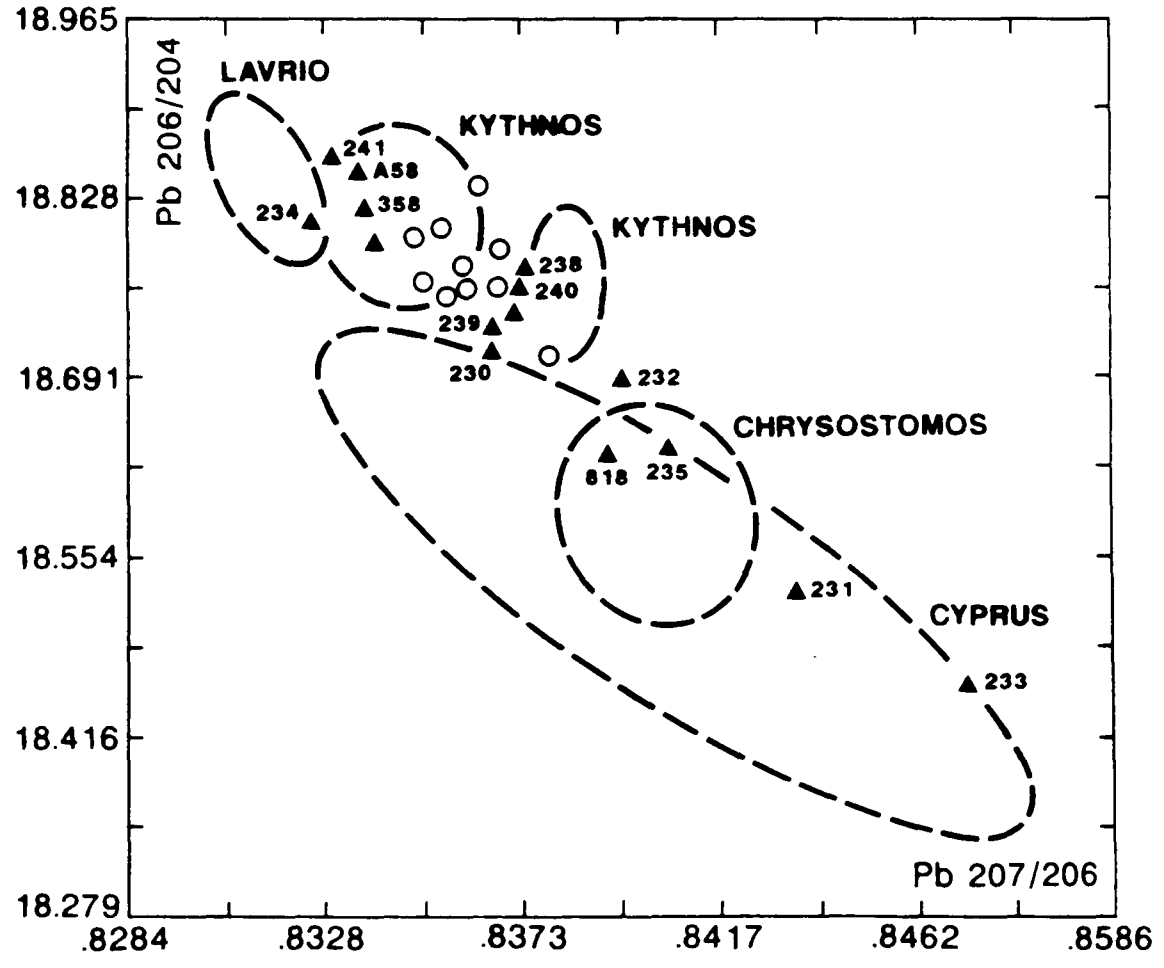
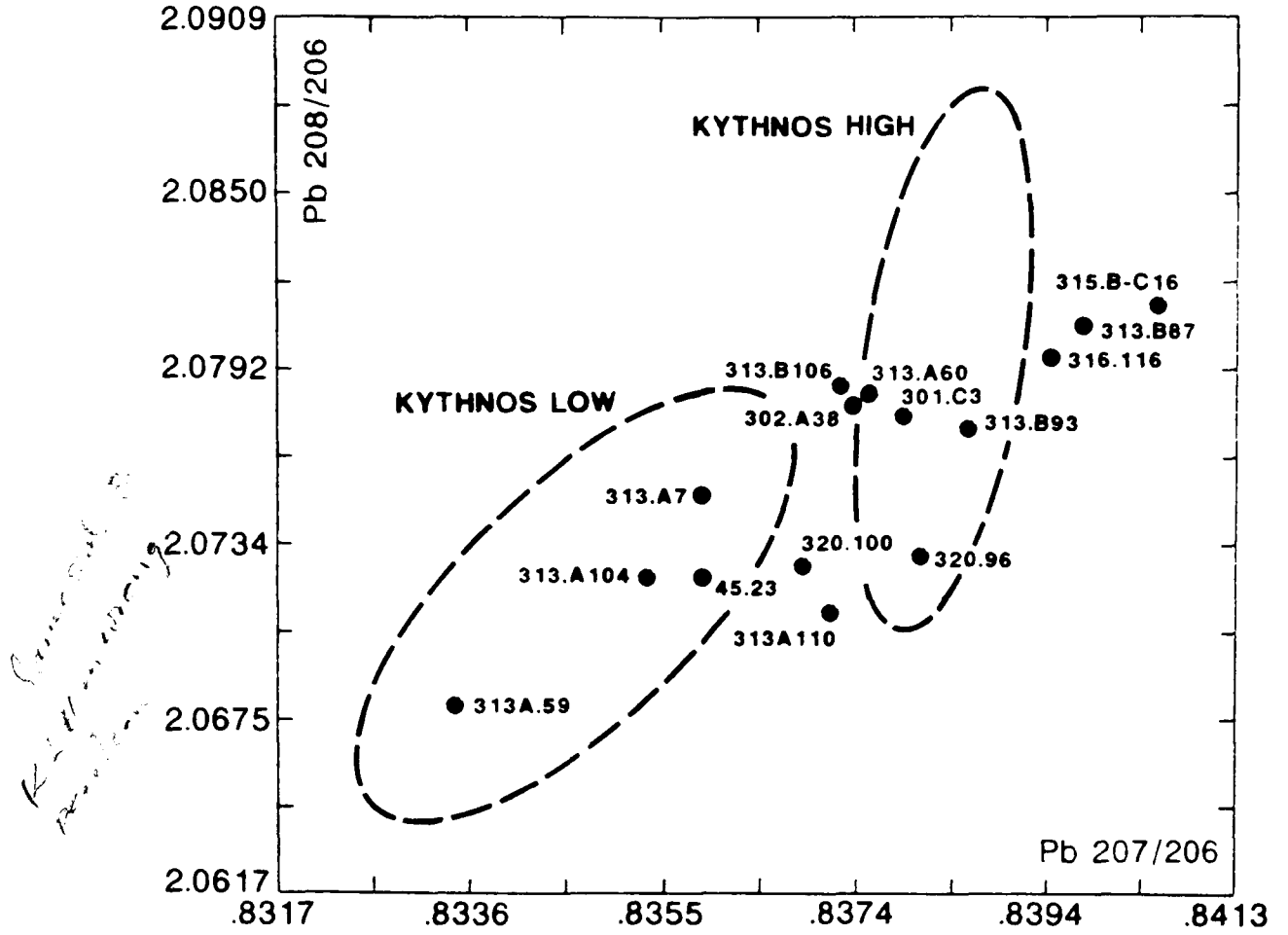


Fig. 35. Lead isotope compositions of the Early Bronze Age Cycladic weapons. The open circles represent weapons from the Kythnos Hoard from the British Museum, black triangles daggers from Amorgos.

Also, in view of the archaeological evidence of possible contacts between Crete and Cyprus in Early and Middle Minoan times (Branigan 1974), it might be interesting to compare the Aegean weapons with Early and Middle Cypriot weapons. In the collection of the Isotrace Laboratory we have a large number of Early Bronze Age Cypriot objects from the Archaeological Museum in Stockholm. Forty two early Cypriot weapons were analysed, and from this number fifteen artefacts have lead isotope compositions consistent with the Cycladic and Cretan weapons. Cypriot copper metallurgy reached its highest point in the last centuries of the 2nd millenium BC; in particular the extensive production of huge (20-30 kg) copper 'oxhide' ingots seems to be a Cypriot monopoly at that time (Gale 1991). It does not follow, however, that in the earlier part of the Bronze Age there was no copper production on Cyprus. A number of objects from the Middle Cypriot site of Alambra in central Cyprus and of EC copper artefacts from the cemeteries of Lapithos and Ayia Paraskevi are indeed consistent with their origin from Cypriot copper (Oxford data, publication in progress). However, the lead isotope data of the fourteen weapons from Lapithos and one dagger from Vounous indicate that perhaps some of the metal produced on the Cycladic islands was also used to make Early Cypriot daggers which were excavated on Cyprus. Table 9 lists the artefacts with lead isotope compositions falling very near the Minoan and Cycladic weapons. On the other hand, some of them (for example, 320.96, 45.2 and 313.B93) are also on the edge of the large Cypriot lead isotope field and the mean lead isotope values of the whole group are much closer to the Cypriot ores than to the Cycladic. Perhaps at present the possibility of the origin of these Cypriot weapons from the same source as the Minoan and Cycladic objects should be treated cautiously. This is a typical case where trace elemental analyses combined with lead isotope data might help to differentiate between the objects. Figure 36 shows the lead isotope compositions of the Cypriot weapons compared with the Cycladic reference 'fields'.

Table 9. Lead isotope data of the early Cypriot weapons.

Object number	Chronology	Site	Description	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb	Origin
302:A38	EC3B	Lapithos	Dagger, Rat-tang	2.07864	.83740	18.733	Kythnos high
301:C3	EC3B	Lapithos	Sword	2.07775	.83793	18.776	Kythnos high
313:A110	MC1	Lapithos	Axe	2.07126	.83723	18.706	Kythnos high
313:B106	MC1	Lapithos	Axe	2.07860	.83751	18.754	Kythnos high
316:116	MC1	Lapithos	Axe	2.07986	.83945	18.718	Kythnos high
320:96	MC1	Lapithos	Axe	2.07323	.83816	18.696	Kythnos high
313:A104	MC1	Lapithos	Dagger	2.07239	.83543	18.715	Kythnos low?
313:A60	MC1	Lapithos	Dagger	2.07861	.83761	18.747	Kythnos high
313:A7	MC1	Lapithos	Dagger	2.07513	.83594	18.728	Kythnos high
313:B87	MC1	Lapithos	Dagger	2.08046	.83974	18.704	Kythnos high
315:B-C16	MC1	Lapithos	Dagger	2.08160	.84050	18.720	Kythnos high
320:100	MC1	Lapithos	Dagger	2.07277	.83700	18.723	Kythnos high
313:B93	MC1	Lapithos	Dagger, Rat-tang	2.07734	.83861	18.702	Kythnos high
313:A59	MC1	Lapithos	Dirk, Rat-tang	2.06801	.83351	18.787	Kythnos low
45:23	EC2	Vounous	Dagger	2.07236	.83595	18.697	Kythnos ?



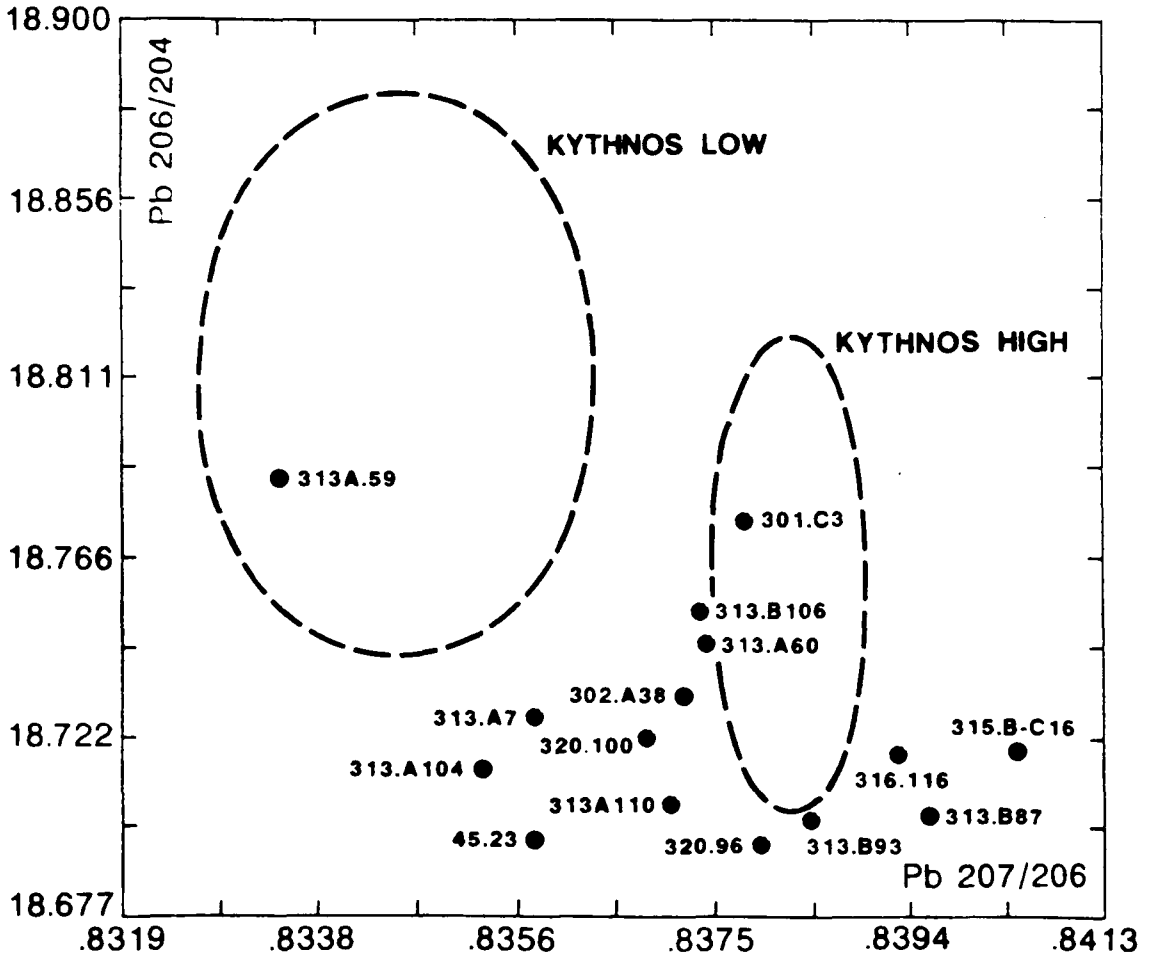
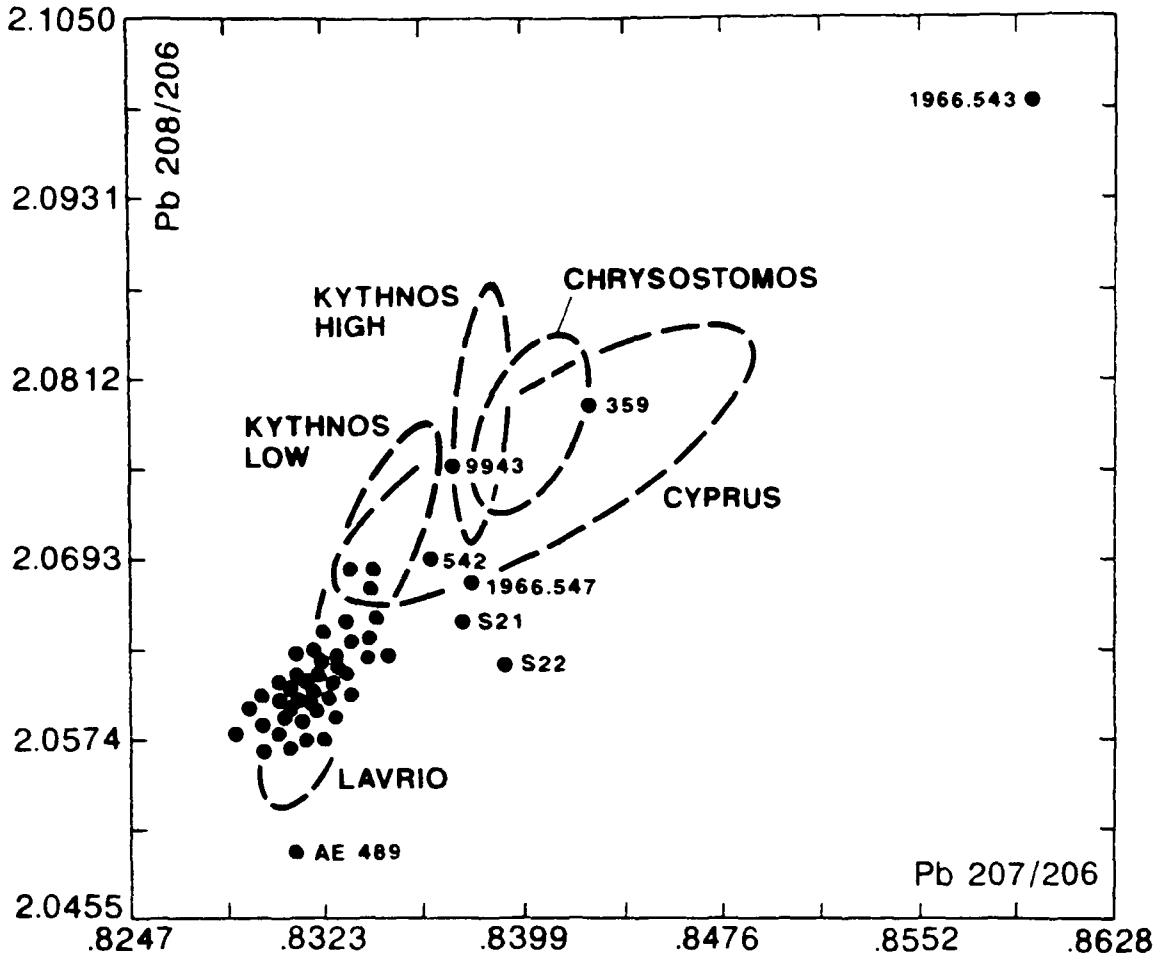


Fig. 36. Comparison of the fields of Cycladic copper slags and ores with lead isotope compositions of the early Cypriot weapons.

7.9. Lead isotope analyses of the Late Bronze Age Minoan weapons.

At the beginning of the Late Bronze Age, in LMI, the wave of destructions marked a significant change in the Minoan culture. This period in Aegean prehistory coincides also with the devastating eruption of the volcano on the island of Thera (Santorini) which in turn might have contributed to a significant change in the sea trade routes. Also, Rutter (1984) argued that somewhat earlier, at the very end of the Early Bronze Age, there was a marked break in the Cycladic culture. Is it possible that this was also the end of the metal production on these islands? The results presented in the previous chapters show that in the earlier periods of the EBA, in all probability, the Cyclades were a major supplier of metal to Crete and also to other regions of the Aegean. The only analysed metals from the latest phase of the Early Cycladic period (ECIII) from Kastri on Syros, are consistent with their origin in Anatolia (Stos-Gale and Gale 1984). The next Aegean disaster came in the 16th century BC with the eruption of the volcano on Thera. Would the " ECIII gap", destruction of Early Minoan Crete and the eruption of Thera be reflected in the origin of metal used on Crete in the Late Minoan periods?

Forty five Late Minoan weapons were analysed for their lead isotope composition to establish the origin of copper used for their production. Figure 37 shows the bivariate plot of the results of analyses in the same configuration as for the early Minoan weapons (Figure 33). The difference between Figures 37 and 33 is quite striking. The lead isotope analyses show that the Late Minoan weapons group mostly in the area of the lead isotope diagram consistent with the ores from Lavrion. The lead isotope data are listed in Table 10. Statistical analysis of the data (Appendix 3;C) shows that 36 out of 45 analysed weapons originate from Lavrion with probabilities ranging from 20 to over 90 percent. This dramatic change in the source of copper supply needs closer archaeological scrutiny, but generally supports the archaeological conclusions about the



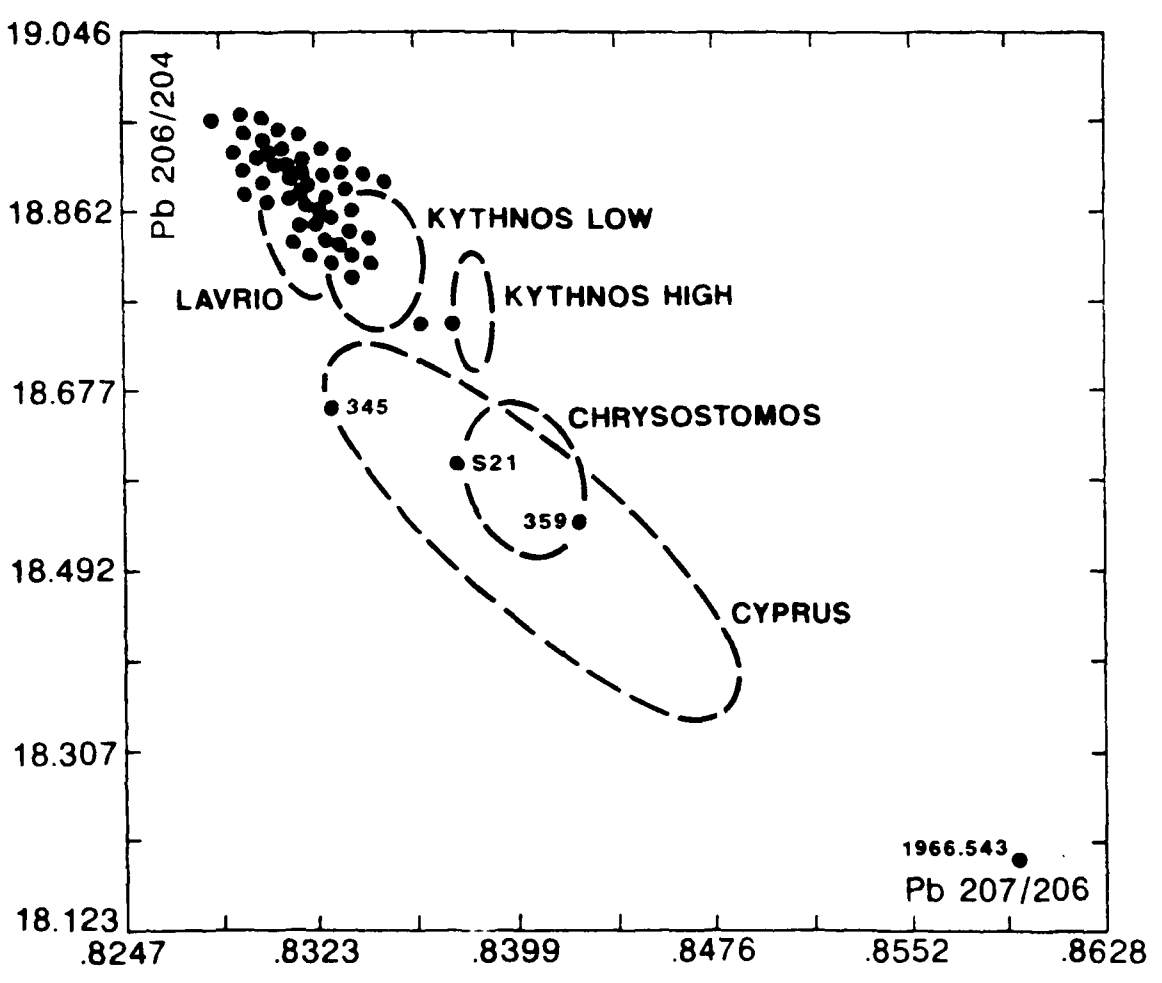


Fig. 37. Lead isotope compositions of the Aegean copper ores and Late Minoan weapons.

increasing linkage of Crete to the Mycenean mainland in the Late Bronze Age

7.10. Lead isotope-based conclusions about the sources of metal used on Crete in the Early to Middle and Late Bronze Age.

During the third Thera Conference, Malcolm Wiener examined the proposition that at the time of the Thera eruption (c. 1550 BC) the sites in the Cyclades, the Dodecanese and other small islands along the coast of Asia Minor constituted complementary parts of a Minoan empire. Lead isotope analyses of the pre-LMI weapons from Crete and the Cyclades show that the great majority of the copper metal is consistent with the lead isotope 'fingerprint' of the Early Bronze Age copper slags and ores from the Cycladic island of Kythnos, with copper slags from Seriphos and with the ores from Siphnos. Some metal seems also consistent with an origin from the copper occurrence of Chrysostomos near the Mesara Plain in Crete, and three objects are made from metal possibly imported from Northern Turkey. Copper from Lavrion is practically absent amongst the Early and Middle Minoan weapons.

Copper occurrences on the Cycladic islands are quite small and their presence was confirmed only on a few of them (Kythnos, Seriphos, and Siphnos). At present, there is nothing known with certainty about the origin and date of the copper slags found on Kea, Seriphos and at Chrysokamino on Crete. However, a possibility exists that in spite of the comparative scarcity of copper ore in the Cyclades the Minoan state provided the right environment for skilled early Bronze Age metallurgists to carry on an efficient and ample copper production on Cycladic islands. We still know very little about the organisation of metallurgical operations in the Mediterranean in the initial phase of the Age of Metals. It is not unusual though, in historical times, to bring ores to a well sited and equipped smelter, rather than necessarily to smelt metal near the mines. Even in rich mineral deposits like Lavrion in the 4th century BC silver was smelted

Table 10. Lead isotope compositions of Late Minoan weapons.

BMDP No.	Object number	Chronology	Site	Description	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb	Origin
1	9943	EMI-LM	Aghios Onufrios	Dagger	2.07555	.83737	18.758	Kythnos high
2	71-A37	LM IIIA:1	Armenoi	Spearhead	2.06279	.83177	18.883	Lavrio
3	71-A52	LM IIIA:2	Armenoi	Spearhead	2.05659	.83112	18.819	Lavrio
4	73-A128	LM IIIA:2	Armenoi	Spearhead	2.06263	.83081	18.927	Lavrio
5	73-A193	LM IIIA/B	Armenoi	Sword	2.06795	.83327	18.905	Kythnos low
6	84-M29	LM IIIB:2	Chania, Kastelli	Arrowhead.	2.06760	.83199	18.866	Kythnos low
7	AE 489	LMIB	Knossos	Sword	2.05052	.83128	18.815	Lavrio
8	AE 491	LMIB	Knossos	Spearhead	2.05867	.83135	18.801	Lavrio
9	AE 492	LMIB	Knossos	Spearhead	2.05964	.83226	18.804	Lavrio
10	2076	LM	Knossos, House B	Double axe	2.06039	.83130	18.885	Lavrio
11	2077	LM	Knossos, House B	Double axe	2.06657	.83361	18.773	Kythnos low
12	2078	LM	Knossos, House B	Double axe	2.06506	.83174	18.864	Kythnos low
13	2080	LM	Knossos, House B	Double axe	2.06757	.83375	18.878	Kythnos low
14	EDB	LM IA	Knossos, NW House	Dagger	2.05868	.82973	18.944	Lavrio
15	2972	LM	Knossos, Sellopoulo T.4	Spearhead	2.06041	.83024	18.887	Lavrio
16	2974	LM	Knossos, Sellopoulo T.4	Spearhead	2.06149	.83350	18.751	Lavrio
17	MUM/72/338	LM II	Knossos, Unexplored Mans.	Spearhead	2.06486	.83335	18.792	Lavrio
18	MUM/72/357	LM II	Knossos, Unexplored Mans.	Spearhead	2.06169	.83067	18.887	Lavrio
19	MUM/72/358	LM II	Knossos, Unexplored Mans.	Spearhead	2.05779	.83034	18.970	Lavrio
20	MUM/72/416	LM II	Knossos, Unexplored Mans.	Dagger	2.06194	.83206	18.887	Lavrio
21	1099	LM	Knossos, Zapher Papoura	Sword type Di	2.06398	.83281	18.812	Lavrio
22	1100	LM	Knossos, Zapher Papoura	Sword type Di	2.06037	.82946	18.931	Lavrio
23	1110	LM	Knossos, Zapher Papoura	One-piece spearhead	2.06299	.83215	18.878	Lavrio
24	1114	LM	Knossos, Zapher Papoura	Long knife	2.06034	.83111	18.885	Lavrio
25	1556	EM/LM	Mochlos	Dagger	2.05892	.83206	18.812	Lavrio

Table 10. continuation ...

BMDP No.	Object number	Chronology	Site	Description	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb	Origin
26	NK 1	MM III?/LM	Nerou Kourou	Double axe	2.06186	.83168	18.853	Lavrio
27	NK 2/75-357-M1	LM I	Nerou Kourou	Double axe	2.05794	.82883	18.913	Lavrio
28	NK 3/76-350-M4	LM I	Nerou Kourou	Sword	2.06210	.83389	18.821	Lavrio
29	NK 4/76-359-M3	LM I	Nerou Kourou	Spearhead	2.05638	.83023	18.859	Lavrio
30	1359	EM/LM	Palaikastro	Long dagger	2.07993	.84257	18.550	Cyprus
31	1038	MM-LM	Phaistos	Axe/adze	2.06230	.83260	18.840	Lavrio
32	1771	MM-LM	Phaistos	Double axe	2.06354	.83290	18.789	Lavrio
33	343	MM-LM	Phaistos	Double axe	2.05693	.82792	18.965	Lavrio
34	344	MM-LM	Phaistos	Double axe	2.06043	.83167	18.854	Lavrio
35	345	MM-LM	Phaistos	Double axe	2.06142	.83291	18.674	Cyprus/Lavrio
36	346	MM-LM	Phaistos	Double axe	2.05870	.83050	18.875	Lavrio
37	347	MM-LM	Phaistos	Double axe	2.05860	.82936	18.937	Lavrio
38	349	MM-LM	Phaistos	Double axe	2.05936	.83048	18.885	Lavrio
39	351	MM-LM	Phaistos	Spearhead	2.06228	.83258	18.841	Lavrio
40	PIG-180	LM IIIA	Pighi	Sword	2.05758	.82918	18.864	Lavrio
41	SAM-F/M222	LM IIIB?	Samonas	Double axe	2.06277	.83922	18.835	Lavrio
42	SAM-G/M221	LM IIIB?	Samonas	Double axe	2.06542	.83764	18.600	Cyprus
43	1966.542	LMIII	Siteia	Sword	2.06984	.83646	18.756	Kythnos low
	1966.543	LMIII	Siteia	Sword	2.10010	.85960	18.200	
44	1966.547	LMIII	Siteia	Spearhead	2.06800	.83819	18.678	Lavrio

only on a few sites (e.g. Panormos, Pefkos) and the ores were brought there from many different mines. This process of setting smelters and bringing the ore to them not only from the nearest occurrence might have started much earlier.

These results seem to agree very well with the evidence accumulated by Wiener and also support strongly the conclusion of Warren that: "... At the very least we can postulate ... a strong degree of linkage, economic and perhaps populational, between the Cyclades and northern Crete in full EB1 or transitional EB 1/2." (Warren 1984, 60). It is not impossible that this period was the beginning of a Cycladic-Minoan metallurgical cooperation, so that the availability of copper for the Minoan smiths was organised in close proximity to Crete and not left to occasional imports from various sources. By the end of the Early Bronze Age a quite extensive metal smelting industry seems to have been organised amongst the Cycladic islands with possible state protection and assured demand from the Minoans. More lead isotope analyses of EBA metal from the Eastern Aegean can provide evidence of the geographical range of export of the copper from Cyclades. In the early part of the Bronze Age some of it might have found its way as far north as Lesbos and Lemnos. There is also a possibility that some of this metal reached even Cyprus. It seems likely that the Minoans organised a quite extensive metal industry at the end of the Early Bronze Age. The comparative lack of metal resources in Crete itself perhaps did not matter too much at this early phase of metal-using society, but the development of craft specialisation and state protection might have been decisive factors in establishing the metal production on the Cyclades. There is also evidence for production of lead and silver in the Cyclades and its use on Crete in the Early Bronze Age (Gale and Stos-Gale 1981). But even more interesting in this context might be another conclusion drawn from the lead isotope analyses of litharge - a by-product of silver extraction - found in EM to LMI contexts on Kea and Thera (Stos-Gale and Gale 1990). Again it seems that the extrac-

tion of this precious metal was very well organised by the state: the silver ore (or silver-rich lead) was brought from Lavrion to houses inside the settlements, where the final extraction took place.

All this lead isotope evidence indicates that across the eastern Aegean, from the northern islands of Lesbos, Lemnos and the Cyclades to Crete, and may be even to Cyprus, copper was being transported from a few central smelting sites, located perhaps on the islands' cliffs. There is little doubt that some Anatolian copper also found its way into the Aegean, but on the present evidence, the importance of the metal from mainland Anatolia was marginal. Much more archaeometallurgical and geological fieldwork on the Cycladic islands is still needed, and many lead isotope and elemental analyses, to solve the puzzle of copper slags and ores on these islands, and to confirm the hypothesis of the origin of the early Minoan and Cycladic copper artefacts, but at least lead isotope analysis provides the means of objective scientific characterisation of ores, metal, slag and each individual archaeological piece of metal for such study.

The number of examples of Early and Middle Minoan metalwork is quite imposing, but the amount of copper-based metal (predominantly tin-bronze) in Late Minoan Crete is staggering. The exhibition in the few rooms of the Heraclion Museum shows only a fraction of what has been excavated on this island and this is amazing enough: enormous bronze axes, saws, cauldrons, swords and tools are crammed in and around the glass cases. Much more is stored in the basement and distributed amongst other museums and private collections. This great increase in the quantity of metal displays a very efficient production of copper and easy access to tin, which must have been imported from beyond the Aegean. In the past, most archaeologists argued that the wealth of LBA bronze on Crete was the result of the contemporary large scale production of copper on Cyprus. In this light, the results of lead isotope analyses of the Late Minoan weapons are very surprising, because only a very small number of objects

are made of copper from Cyprus. The dominant source of metal seems to be the multimetallic deposit of Lavrio in Attica. The importance of this deposit for Bronze Age Greece cannot be overestimated. Unfortunately, later exploitation of the mineral resources in the Lavrio region (mostly for silver and lead) destroyed completely, as it seems, most traces of the earliest activities. The only indication so far of the Bronze Age exploitation of the ores in Lavrio is the Mine in Thorikos excavated by the Belgian archaeologists (Spitaels 1984). Even now, however, rich copper minerals in Lavrio are easy to find. They are certainly much more economic for large scale copper smelting that the small occurrences in the Cyclades or Crete. In view of the close links of the Early Bronze Age Cretan state with the Cyclades, Lavrio is only a step away from the Minoanised Kea and the string of islands leading to Crete. It is possible that the intensification of the production of metals from Lavrio in the Late Bronze Age was a direct extension of the EBA Cyclado-Minoan metallurgical network adapting to the increase in demand and stronger links with the Mycenean mainland. The archaeological survey of southern Attica by German archaeologists revealed a network of Mycenean roads and watch-towers (papers given at the 6th International Colloquium on Aegean Prehistory, Athens, September 1987). Archaeological evidence of this type combined with the results of a large-scale lead isotope research project might prove very important in the reconstruction of the history of the economy of the Bronze Age Aegean.

To date we have analysed several hundreds of copper-based artefacts from Minoan Crete in the framework of the British Academy project and the small number of artefacts made of Cypriot copper is quite obvious. Over a hundred of these objects are at present being analysed for their chemical composition by Mrs. H. Magou of the National Archaeological Museum in Athens and all will be fully published in collaboration with her and other members of the Greek Archaeological Service and British archaeologists. However, even this preliminary

interpretation of the lead isotope data shows that there is no other scientific or archaeological method which could so clearly distinguish the different origins of metal from which were fashioned very similar, or even ostensibly identical, artefacts made and found in the same geographical area.

8. LEAD ISOTOPE ANALYSES OF METAL OBJECTS FROM A SITE OF ROMAN PERIOD IN SOUTHERN POLAND.

8.1. Mining and metallurgy in Europe in the Roman period.

In the first millenium BC, the importance of bronze in European metallurgy declined gradually, while iron took the place of bronze as the most widely used metal. During the Roman period, all over Europe weapons and tools were chiefly made of iron; the copper alloys were largely used for production of vessels, statues and small decorative objects. At the same time, the tin bronze became less common and the range of different copper alloys increased. Greek authors speak of a new metal being used in Asia Minor from the 7-8th century BC - this metal was a copper-zinc alloy (brass). The method of brass making was known to the Etruscans from the 5th century BC and from then on spread throughout the Roman Empire. By the first century BC the Roman mints were producing series of brass coins with a very uniform composition of 21% to 25% of zinc (Craddock et al. 1980). However, the other "bronzes" of Roman period show very varied compositions. A recent metallurgical study of over 400 Gallo-Roman "bronzes" shows that the majority of objects is made of quaternary alloys (Cu-Sn-Zn-Pb) with mean values for Sn 7.7%, Zn 10% and Pb 10.7%, but the range of each of these elements in particular objects is very wide - from less than 0.5% to over 20% (Beck et al. 1985, 90, Fig 4.).

The reasons for the change from tin-bronze to brass are quite easy to understand: brass has metallurgical qualities similar to tin bronze, but zinc minerals are more common than tin in the European mineral deposits. Additionally, zinc minerals are most often associated with copper, silver and lead, therefore all components of a good copper alloy (Cu-Zn-Pb) can be mined and smelted in one region. The most important tin deposits in Western Europe are in Cornwall

and Spain; smaller occurrences were exploited in antiquity in Britanny, Tuscany and possibly Sardinia. All these resources had been in use for nearly a thousand years before the Roman period; possibly the tin production was no longer very efficient in the three latter areas. In central Europe, large tin deposits are in the Erzgebirge, but these mountains were beyond the borders of the Roman Empire.

It is very likely that the Greeks and Romans had no direct knowledge of zinc, which, being very volatile at the temperature at which it is reduced from its ores, has to have furnaces provided with suitable distillatory and condensing apparatus. On the other hand, when minerals containing zinc are heated in a furnace, the vapour of zinc may be accidentally condensed in cracks in the walls of a furnace and trickle down in drops (Percy 1861, p.519). This process might have led to an accidental production of brass during copper smelting, and, once the process of brass making was established, this alloy could have been made in many European localities from minerals available in one area. In Roman times brass was made by the process of cementation (Craddock et al. 1980). During the cementation, calcined zinc oxide and carbonate ores were reduced by heating with charcoal in a closed crucible in the presence of finely grained copper metal, which absorbed the zinc as it formed. The temperature of this operation must have been carefully controlled and maintained at $950-1000^0$C to prevent copper from melting. The chemical analyses of Roman and later metals show that pure brass was not very often used; a great majority of the alloys contains also lead and tin. The presence of lead can be explained either by the use of zinc minerals, or copper metal, containing some lead, or the lead could have been added separately to the final alloy. Tin is not very likely to come from any of the minerals used for copper or brass production, but might be present in copper, if, instead of pure copper, scrap bronze was used for the brass making. Alternatively, pure tin (or scrap bronze) might have been deliberately added to the final alloy.

On the present evidence, the extraction on a large scale of zinc metal in pure form at the beginning of our era seems highly unlikely. In historical times pure zinc was for the first time brought to Europe from the East Indies by the Portuguese in the XVIII century. Shortly afterwards, the English and Germans began the European production of zinc (Percy 1861, p.519). Craddock et al. (1980) have demonstrated that a typical zinc content resulting from the process of cementation is below 28%, and, indeed, higher zinc content in the metals from the first centuries AD is very unusual.

The vast area of the European part of the Roman Empire included mines of all metals used at that time, and it is quite certain that all types of metals were produced on a large scale under the Roman patronage. Copper, lead and zinc mining in the Roman Empire was marginal in comparison with the exploitation of gold and silver and the production of iron.

The history of Roman mining and metallurgy, based predominantly on the ancient texts, was well summarised by Healy (1978). The entry for the Roman sources of copper (Healy 1978, 58-59) includes Spain and Southern France, Tuscany, Sardinia, Cyprus and Britain. The Roman writers do not seem to mention as copper sources the large deposits in South-West Germany (Schwarzwald), along the Rhine and in the Austrian Tyrol, where most certainly this metal was extracted. Zinc (p.65) minerals were known in Gaul, Northern Italy, and on the left bank of the Rhine. The large zinc/lead deposits of Sardinia are not mentioned. Britain is quoted as a major source of lead under the empire, much lead having also been mined at that time in Spain; Gaul is mentioned again, but Sardinian deposits, which were certainly worked by the Romans, are not mentioned by Strabo or Pliny (Healy 1978, 61). The comparison of the ancient records with the geological information available today indicates that the Roman writers might have missed some of the mining and metal production centers in more remote provinces. Davis (1935) has also noticed that some of

the mineral 'occurrences' mentioned by Pliny (for example in Sicily) could not have been confirmed. The comparative lack of interest in mining amongst the Roman writers is quite understandable, because within the Roman class system manual workers belonged to the lowest category and mining must have been at the bottom of the scale. One can imagine that the general interest of the population of Rome in industrial production was rather limited.

More information about the Roman mining and smelting industry in Europe can be found in the account published by Oliver Davies (1935), who supplemented the ancient records with a substantial amount of field work. Unfortunately, his research seems to be centered heavily on the Mediterranean and his comments on the Roman exploitation of the German and Austrian metal deposits are chiefly based on literature. According to his research the major copper mining districts of the Roman period were in North-West Italy, Spain, France and Greece. Some of the mines in the British Isles, particularly in the lead and tin deposits, were also active at that time. In Central Europe, the Romans exploited the mineral deposits on both sides of the Rhine and along the Middle Danube, reaching south to Illyria, Moesia and Macedonia (Davies 1935). Towards the eastern borders of the Empire, the important mineral deposits utilised by Romans were in the mountains west of the Rhine (between Cologne and Mainz). The metals mined there were silver, lead, copper, and (above all) iron. The Romans in the first century AD mined also at some distance beyond their normal civil frontier (Davies 1935, 179). In the region of Ems, on the east side of the Rhine near Koblenz, there are many pre-Roman and Roman mines; the ore is argentiferous lead, with some copper and iron. Zinc minerals also occur in these locations in association with copper, lead and silver. The main Roman interest in this area was the recovery of silver, but on a Roman site near Braubach some copper slag was also discovered.

Further south are the rich deposits of iron, copper, lead, silver and gold in

the mountains of Austria. It is certain that the copper was mined in Austria since prehistoric times and the Celts developed there an extensive iron smelting industry. In 15 AD the Romans extended their border to the Danube and considerably developed the mining of gold and silver (Holzer 1986). The Romans most certainly mined also copper, lead and silver in the Rhodope and the Balkans, but there was probably no Roman mining further east and north from the Transylvanian Metalliferous Mountains, because the Romans did not reach beyond the Danube.

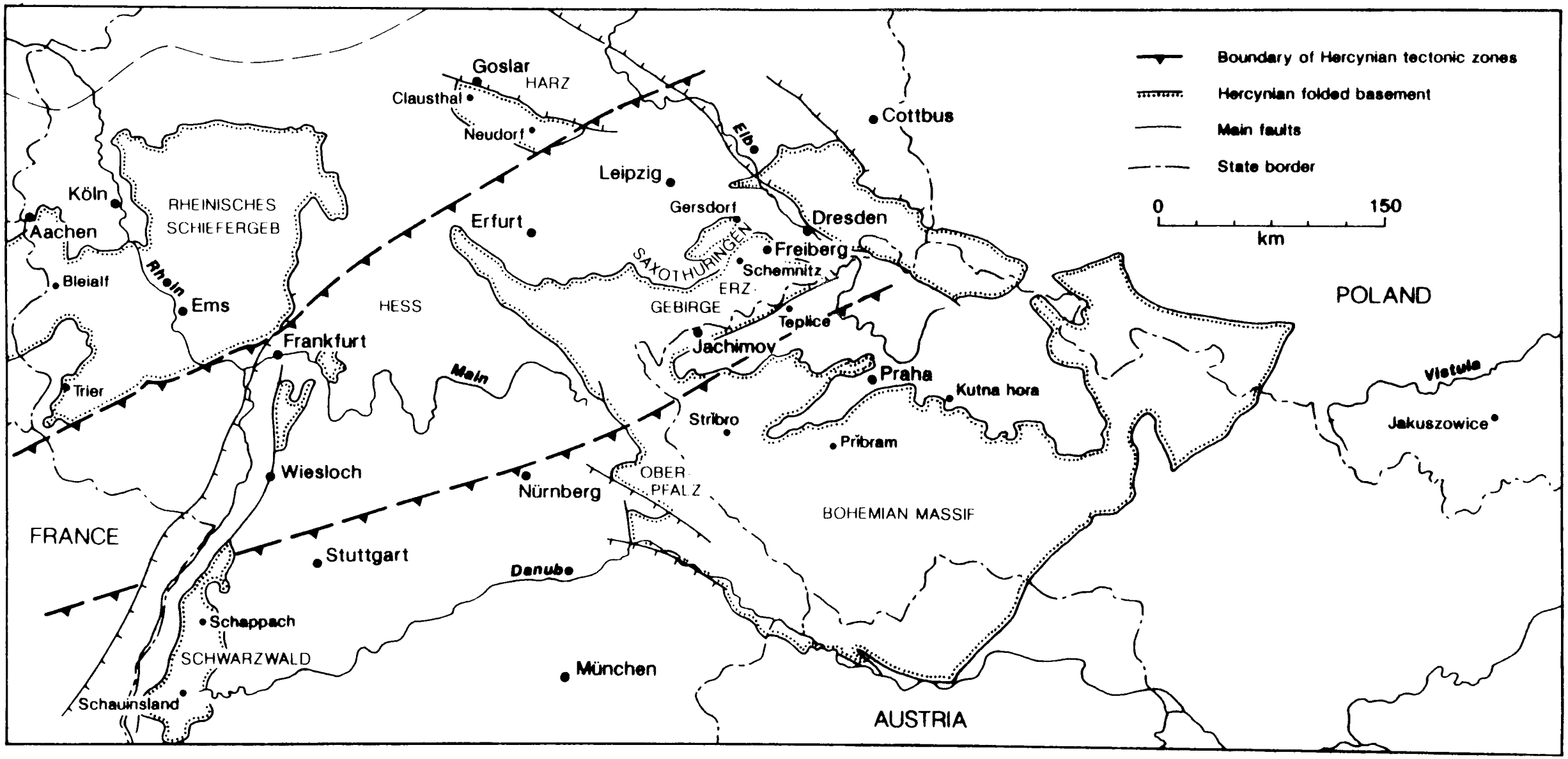
Several large and rich European multimetallic deposits were situated outside the borders of the Roman Empire (for example the Harz Mountains and the Bohemian Massif, including the Erzgebirge - see Figure 12 for their geographical position). Some of them must have been exploited in the Bronze Age and in Celtic times, but practically nothing is known about the metal production from these ores in the first centuries of our era. Since there is no mention of this matter in the Roman texts, and the field evidence is hard to find owing to the extensive Mediaeval mining of these deposits, archaeologists accepted the idea that all metal used in central Europe in the Roman period, came from imported Roman objects (coins?) or scrap. This theory also gains support from the present archaeological evidence, which implies that the European tribes living outside the Roman Empire did not have, at that time, the social organisation which could support their own production of metals.

Looking at this problem purely from the geological point of view, it might seem strange that the production of metal in such mineralogically rich deposits as the Bohemian Massif (see Figure 38), would cease completely after the long period of Bronze Age and Celtic activity. These mountains are rich in gold, silver, tin, copper and lead and zinc minerals, and there are indications that the Celts exploited placer gold from this area (Pouba and Ilavsky 1986). In the Middle Ages the most famous silver mines were in the Erzgebirge and the

copper, silver and lead mines of Saxony brought great wealth to this part of Europe. Georgius Bauer, better known as Agricola, wrote his famous book *De Re Metallica* in the town of Jachymov/Joachimstahl near the modern Czech-German border, and most of the information about the XVIth century European mining and metallurgy included in his book is based on the local activities. The lack of evidence of Roman period mining might be accidental. It is certain that advanced metallurgy was not totally unknown in *Barbaricum*, which included most of the present day Germany, Bohemia and Poland. For example, in the Swietokrzyskie Mountains in southern Poland there was an extensive iron mining and smelting centre producing large quantities of this metal for local use in the first centuries of our era (Godlowski and Kozlowski 1985, p. 13).

On the other hand, a long hiatus in the mining operations in Central Europe in the first centuries of our era cannot be excluded. The only scientific method available at present, which is capable of providing independent evidence about the origin of metals is the lead isotope technique. Perhaps it can be used for the assessment of the exploitation, or lack of it, of the non-ferrous Central European ore deposits in Roman times? The lead isotope data base on the ore deposits exploited by Romans is not quite satisfactory, but many of them were covered by our Bronze Age project. We also had samples of many ores from Western Germany and some from the Balkans and Poland. Some lead isotope data of the ores from the Central European ore deposits were found in the geological publications. I am very grateful to Dr. Bielicki of Leipzig for letting me use his compilation of over 300 lead isotope data on ores from the Bohemian Massif and Harz. The lead isotope data of ore deposits relevant to Roman metallurgy in Central Europe are listed in Appendix 3. Figure 38 shows the rivers Rhine and Danube which formed the borders of the Roman Empire in this part of Europe and the ore deposits mentioned above.

Fig. 38. The site of Jakuszowice in Southern Poland and the central European ore deposits.



8.2. The Roman period metal workshop on the site of Jakuszowice in Southern Poland.

Metal artefacts from a site in Southern Poland seemed ideal material for testing the possibility of application of the lead isotope technique in the context of Roman metallurgy. Since 1982 the Institute of Archaeology of the Jagiellonian University in Krakow has been involved in a systematic excavation of a multi-period settlement of Jakuszowice situated 50 km north-east from Krakow (Godlowski 1991). The results of the archaeological excavation place this site amongst the most interesting prehistoric settlements in Poland. The pottery finds from the La Tene and Roman periods of the settlement consist of wares associated predominantly with the native Przeworsk Culture, proving its local origins. Jakuszowice is of great importance for Polish archaeometallurgy, because "...it is distinguished from other Roman period settlements in Poland by its extraordinary wealth of material, notably metal." (Godlowski 1991, p. 664). Several workshop areas were identified at Jakuszowice: there was a glass workshop, an amber workshop and an iron smithy. The excavators believe that a primitive iron smelting was also carried out on this site in parallel with reworking of scrap iron (Godlowski 1991, p.672). There is no doubt that Jakuszowice was one of the more important centers of metal working in this region. More than 100 fragments of metal were found there, including many half finished small decorative objects found together with fragments of little crucibles. One of the most interesting finds from this group is a fragment of a well-shaped bar ingot (See Photograph 11, No.110/82), strikingly similar to an ingot which could have been cast in the stone mould from the Isle of Man reproduced by Tylecote (1987, p.19, Figure 1.8). Copper ingots with **V** to **D** shaped sections were quite common since the Early Bronze Age in Central Europe and often found in hoards (Butler 1978, p.351, Fig 2.5). The ingot fragment from Jakuszowice is of a typical Roman ternary alloy of Cu/Zn/Pb and it is a single find

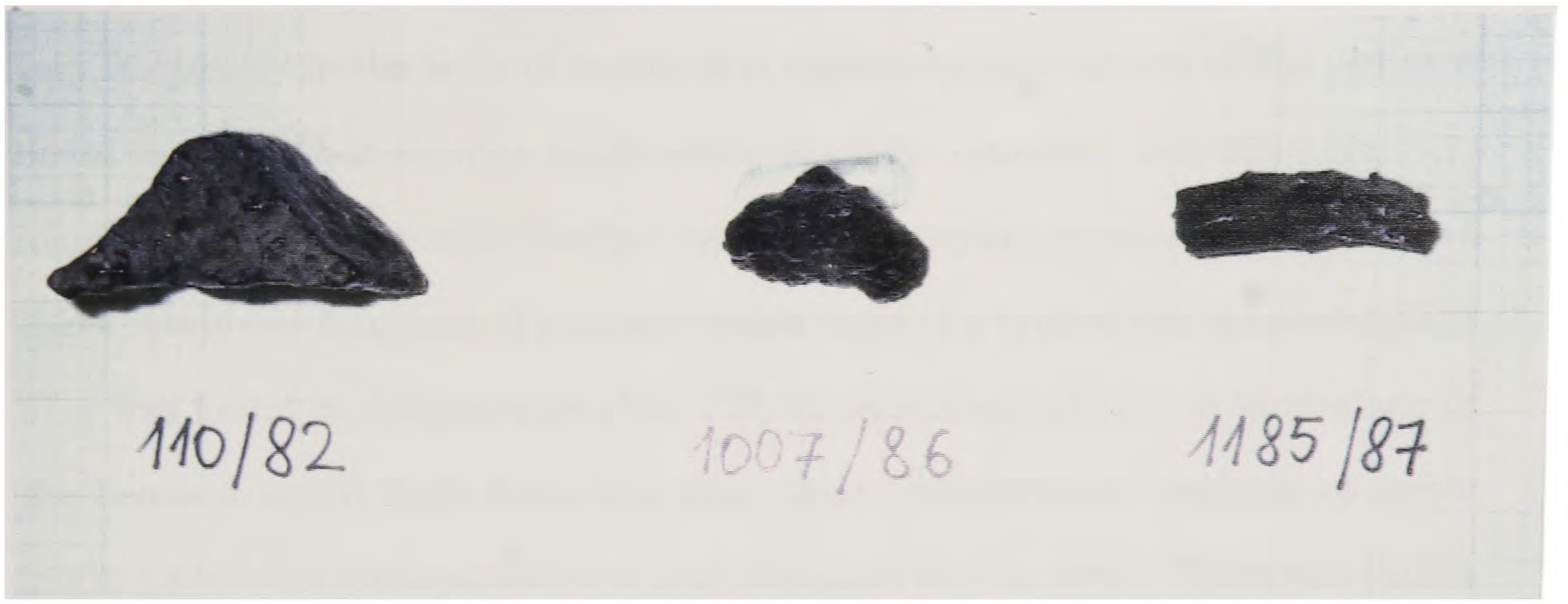
of this type on the site. The stratigraphy of the metal workshop situated on a slope by the river covers several centuries.

The finds from the site of Jakuszowice prove that the inhabitants of this settlement had extensive trading contacts with other parts of Europe. Amongst over 80 fibulae or their fragments recovered so far, there are examples of Celtic (La Tene) designs and a Roman *Zwiebelknopffibel*, which were worn in the 4th century AD by Roman military and civilian officials and are only very rarely found beyond the *limes*. A number of other glass, stone and small metal artefacts are possibly also of Roman origin. Forty-six Late Roman coins (silver denarii) - the largest concentration of Roman coins in settlements from the European *Barbaricum* (Godlowski 1991, 670) - were excavated there in recent years.

The importance of Jakuszowice for the studies of the early history of Poland is perhaps best summarized in the excavator's words: "... The Jakuszowice settlement in the Early and Later Roman periods is strikingly distinct from similar contemporary sites in terms of the intensity of habitation traces, manifested by the thickness of culture-bearing stratifications, and the extraordinary wealth of finds, in particular metal items, Roman coins and various other imports, many of which are unique in Poland. The imports demonstrate how lively and varied were the contacts between Jakuszowice and the Roman Empire, its limes some 300 km away ... it is probable that Jakuszowice was a long standing local centre of economic and social life." (Godlowski 1991, p.673-674).

In view of the archaeological evidence discussed above, it seemed likely that the non-ferrous metals excavated in Jakuszowice might have been imported from the Roman-dominated parts of Europe. So far, the only metal objects identifiable as of Roman manufacture are the coins and the fibulae mentioned above. There is not much evidence of larger metal artefacts, like vessels or statues, which might have been used in the re-melting of Roman metal. Of course the negative evidence does not prove that such objects have never been

Phot. 11. Fragments of ingots from Jakuszowice.



Phot. 12. Crucible from Jakuszowice (hight 35 mm, diameter 40 mm). The XRF of the red 'glaze' on the rim indicated high copper and zinc content.

used as scrap metal. On the other hand, since the Bronze Age metal was traded very frequently in the form of ingots, it is significant that several of the pieces of metal found in Jakuszowice might represent their remains. The most common ingot shapes in continental Europe were bars of varying cross-section and round cakes. Only one fragment of a copper-based ingot of a typical bar shape weighing 87 g was found in Jakuszowice (No. 110/82 mentioned above); it is also one of the heaviest metal finds from this site. Quite considerable amounts of metal might have been transported over long distances in this form. When one thinks about the trade in metal in economic terms, large and oddly shaped vessels or statues are much less convenient for carrying on a horse, or in a cart, than compact small pieces of solid metal, which have shapes fitting neatly and can be easily cut into appropriate size for a transaction. Amongst the copper based metal finds from Jakuszowice three objects in particular seem likely to represent the remains of a stock of raw metal: the ingot fragment, a heavy metal 'button' about 2 cm in diameter and 1 cm in height, and a 2.5 cm long piece of a metal rod with square cross-section. All these three objects are represented on Photograph 11. Such small raw metal pieces would be very useful for the workshop of the Jakuszowice, where the copper smith was making fibulae and small ornaments. The crucibles for melting copper were small (see Photograph 12) and rods and buttons would provide a convenient supply of quantities of metal required for such production. Amongst the metal finds there were also several pieces of silver in the shape of small discs, and pieces of lead including a 'lead ingot'. All these metal 'ingots' might have been made on metal smelting sites (possibly in the region where the metals were mined), or might have been prepared from recycled metal in metallurgical establishments specially for trading purposes. Very little is known about the organisation of the production of copper based metals in the Roman Empire. Nothing at all is known about the organisation of copper metallurgy in *Barbaricum*.

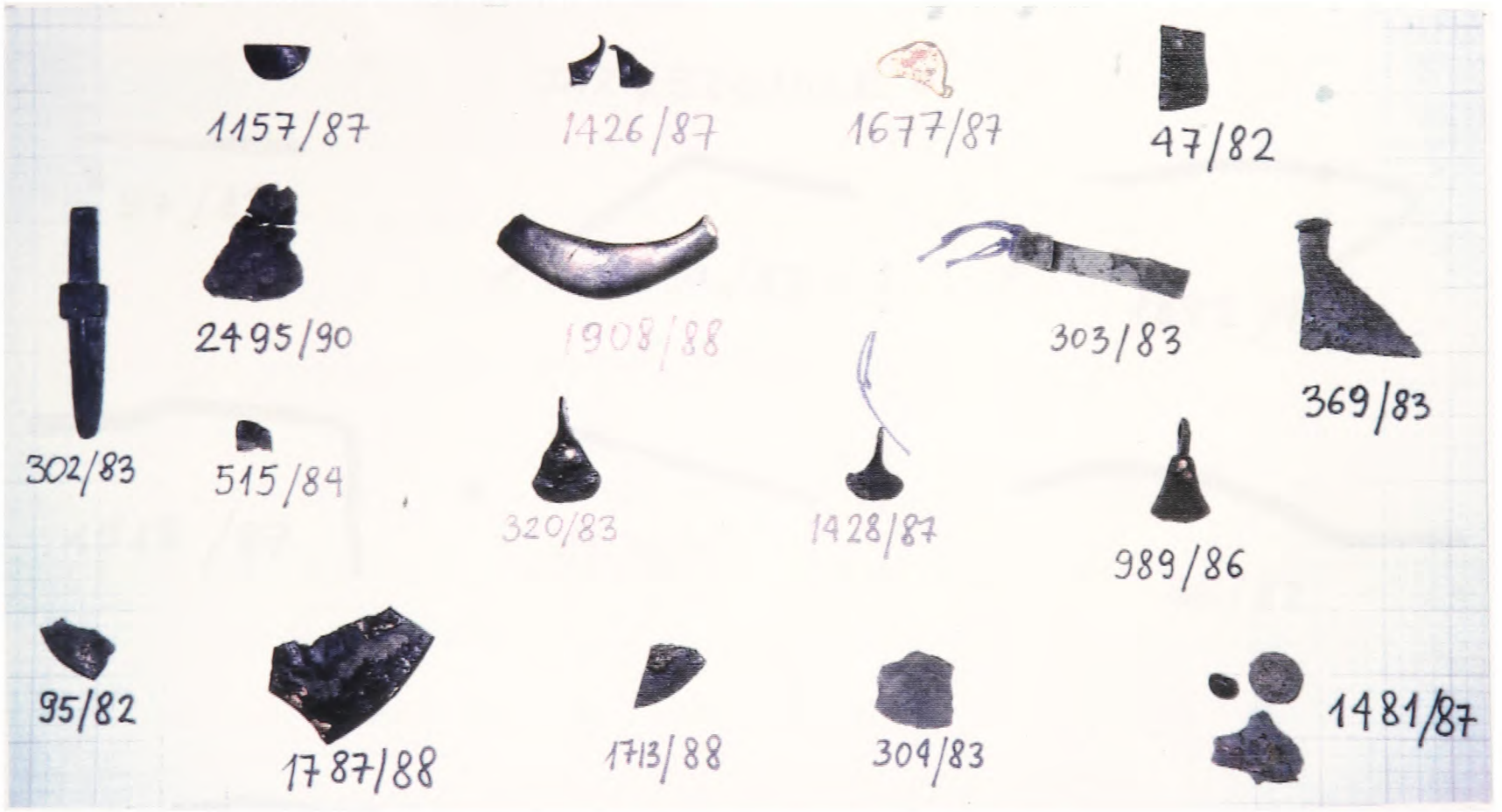
Lead isotope analysis of the metal finds from Jakuszowice seems to be the only chance to find more information about their origins. The success of linking of lead isotope compositions of these metals directly with ore deposits would be limited if the metals were indeed primarily from many different sources, and then repeatedly mixed and remelted, and lead from different locations was added and mixed at various stages. The lead isotope signatures of the final product in such cases would be totally random and artificial in comparison with the ores. On the other hand all (or the majority) of the metals might have been imported to Jakuszowice from only a few mining regions, or even one. The results of our extensive study of the Bronze Age Mediterranean metallurgy show that peoples in certain geographical areas often depended for long periods on the closest or most economical sources of metals. This conclusion might also prove right for the later periods. This work is only the first attempt at finding the ore sources of metals from an archaeological site of a Roman period, within or outside the Empire, and it can be treated as a case study.

8.3. The alloy types of objects from Jakuszowice analysed at Oxford and their comparison with Provincial Roman metals.

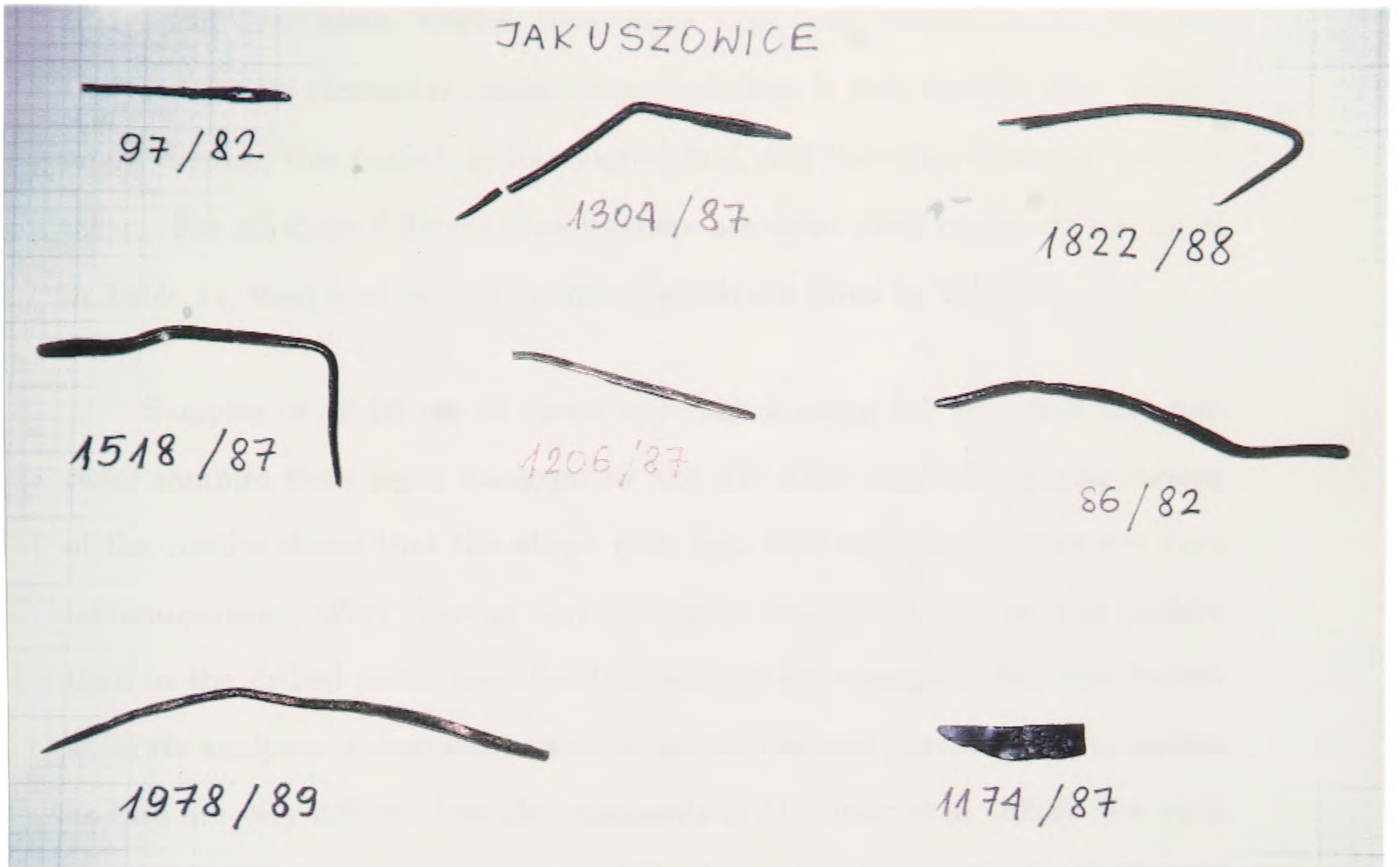
The excavator's selection of metal finds from Jakuszowice was brought to Oxford to be sampled for lead isotope analysis. Also, four objects from a contemporary cremation burial in the near-by village of Opatow were included in this program of analyses (see Photographs 13 and 14). The objects have never before been analysed for their elemental compositions and the metal types were known only from their archaeological description. Since the type of alloy, and particularly the lead content of metal, is very important for the sampling and lead extraction procedures and the final interpretation of lead isotope data, all objects were first analysed for their alloy composition on various points of the surface using the ED XRF system at the Oxford Research Laboratory for Archaeology (Stos-Gale 1986, Mortimer et al. 1986). Some metal inclusions

Phot. 13. Copper based objects from Jakuszowice. Artefact No. 1677/87 is a fragment of gold.

Phot. 13. Copper based objects from Jakuszowice. Artefact No. 1677/87 is a fragment of gold.



Phot. 14. Copper based objects from Jakuszowice and Opatow. Artefact No. 1143/66 is a silver fibulae.



on crucible fragments were also analysed by this method, but no lead isotope analyses of these metal droplets were made. One small fibula (No. 511/84) was analysed for its elemental composition, but then it was decided that drilling might damage this perfect archaeological find, and therefore a sample was not taken. For all these different reasons there are more alloy compositions, given in Table 11, than lead isotope analyses, which are listed in Table 16.

Samples of 10-20 mg of metal were taken using 1.5 mm drill bits and these samples were again analysed by the ED XRF method. A comparison of the results shows that the alloys with high lead and zinc content are very inhomogeneous, often showing a much higher amount of lead on the surface than in the drilled metal (see Nos.110 and 136 for example). For this reason accurate analyses of compositions of alloys with several percent of zinc, copper and tin are very difficult (see also comments in Mortimer et al. 1986). For such metals the XRF analysis can be treated only as a semi-quantitative method of alloy analysis, but it is quite sufficient to provide the information about the metal types and levels of concentrations of the major elements. In some ways the ED XRF analysis of inhomogeneous copper based alloys, and other metals of unknown compositions, has certain a advantage over other commonly used methods of analysis (Atomic Absorption for example): it is very fast (a few minutes per sample), shows simultaneously all elements present in the sample above about 0.1% and it is possible to analyse **non-destructively** many spots of the whole object and therefore check the distribution of different metals. The accuracy of such an analysis is in the region of 10%, but in the case of very inhomogeneous alloys the accuracy of a measurement of a very small volume of the metal is often less significant than the variations in concentrations of different elements of the alloy throughout the artefact. The only really accurate method of chemical analysis of such objects would be for example neutron activation, or complete dissolution, of the **whole** artefact for analysis. Such an approach

Table 11. Alloy compositions of drilled samples of metals from Jakuszowice. In several cases the results of surface XRF analyses are also given for comparison.

Object number	Date	Description	Cu %	Sn %	Zn %	Pb %	Other elements
1007/86	L.Roman	Metal button (weight?)	83.36	4.60	6.64	5.23	Fe
1047/86	L.Roman	Fibula not finished	81.71	.10	16.91	1.25	Fe
110/82	L.Roman	Copper ingot - surface	63.00	.10	18.00	14.00	Fe
110/82dr	L.Roman	Copper ingot - drilling	78.30	.10	16.00	5.40	Fe
1143/66	L.R. 4c AD	Silver fibulae	5.00	.10	.10	.50	Ag 91%, Au 1%
1157/87	L.Roman?	Small disc (13 mm)	80.73	.10	16.11	2.76	Fe
1174/87	L.Roman?	Copper bar	94.83	2.89	.10	1.57	Fe
1185/87	L.Roman?	Bronze rod	84.77	.89	9.26	4.72	Fe
1197/87	L.R./later	Lead, small plate	.28	.10	.10	97.50	Fe
1206/87	L.Roman	Bronze wire, square section	81.57	3.89	6.51	5.74	Fe
1212/87	L.Roman?	Small plate	.10	.10	95.00	4.00	Fe
1275/87	L.R./later	Lead, small plate	.05	.05	.10	99.90	nd
1303/87	E.L.R/2cAD	Bronze fib frgm	50.00	15.00	.10	35.00	Fe
1304/87	E.L.R.?	Bronze needle	73.83	4.96	16.57	3.23	Fe
136/82	L.Roman	Molten bronze fragment-surface	41.00	1.00	36.00	12.00	Fe
136/82 dr1	L.Roman	Molten bronze - drilling	83.92	.10	12.60	2.80	Fe
136/82 dr2	L.Roman	Molten bronze - drilling	80.70	.10	16.20	2.30	Fe
1365/87	L.Roman?	Lead droplet	.10	.10	.10	99.90	nd
1371/87	L.Roman?	Lead droplet	.10	.10	.10	99.90	nd
1390/87	L.Roman?	Metal strip	.59	19.76	.10	79.40	Fe
1426/87 a	L.Roman?	Small triangle of metal	76.65	4.47	8.37	8.71	Fe
1426/87 b	L.Roman?	Small triangle of metal	72.60	3.50	10.27	12.59	Fe
1428/87	L.R. 3c AD	Axe pendant	64.00	.10	15.00	16.00	Fe
1458/87	E.L.R.	Small disc	26.70	2.48	5.40	2.12	Ag 60.9%, Fe
1465/87	L.Roman?	Droplet of metal	81.84	.10	12.44	5.44	Fe
1466/87	L.Roman?	Bronze fragment	88.30	.10	10.09	1.44	Fe
1481/87a	L.Roman?	Metal droplet	87.00	.10	.10	8.00	Fe
1499/87	L.Roman?	Metal droplet	.10	.30	.10	99.60	Ag .12%
1518/87	L.Roman	Needle, half-finished	78.18	.10	19.62	2.92	Fe
1528/87	L.Roman	Fragment of a metal disc	68.20	.10	1.50	1.20	Ag 29%
16/82	L.Roman	Bronze fragment - surface	84.00	.10	.50	15.00	Fe
16/82dr	L.Roman	Bronze fragment - drilling	86.90	.10	5.30	7.50	Fe
1713/88	L.Roman	Piece of a bronze mirror	94.70	3.60	.10	1.45	Fe
174/82	L.Roman	Metal droplet in slag	60.89	.10	12.29	6.28	Fe
1778/87	L.Roman?	Lead	.11	.10	.10	99.80	nd
1787/88	L.Roman	Piece of a bronze mirror	62.39	12.71	.10	24.56	Fe
1822/88	L.Roman	Fragment of a needle	84.92	.64	12.29	.88	Fe
1867/88	LaTD1 1cBC	Fragment of a Latenian fibulae	76.00	10.00	.10	14.00	Fe
1867/88	LaTD1 1cBC	Drilling from the fibulae	49.71	31.60	.10	16.90	As, Ni, Fe
1886/88	E.Roman	Lead ingot (bent rod)	.13	1.87	.10	97.80	Fe
1908/88	L.Roman?	Half-moon plate, golden colour	75.78	.71	18.88	3.44	Fe, Ni
1978/89	L.Roman	Needle, half-finished(surface)	94.00	.10	4.00	2.00	Fe
1978/89dr	L.Roman	Needle, half-finished/drilling	86.40	.10	11.30	2.10	Fe

Table 11. continuation ...

Object number	Date	Description	Cu %	Sn %	Zn %	Pb %	Other elements
2/82	L.R. 4c AD	Bronze fibulae - surface	80.00	.10	.50	19.00	Fe
2/82dr	L.R. 4c AD	Bronze fibulae - drilling	65.00	.10	11.00	24.00	Fe
216/82	L.R. ??	Lead	.10	.10	.10	99.90	Fe
227/82	L.R. ??	Lead	.10	.10	.10	99.90	Fe
229/82	L.R. ??	Lead	.10	13.20	.10	86.50	Fe
2495/901	L.R. 3c AD	Large axe pendant	77.99	.10	18.76	2.63	Fe
2495/90s	L.R. 3c AD	Large axe pendant	77.66	.10	14.17	5.92	Fe
278/83	L.R.	Metal droplet on a crucible	62.25	.10	25.72	4.70	Fe
280/83	E.Roman	Corroded plate - surface	48.00	41.80	.10	8.90	Fe
280/83	E.Roman	Corroded plate - drilling	62.20	23.10	.10	14.00	Fe
302/83	L.R. 4-5 c	Fragment of a buckle - surface	88.00	.10	1.50	8.00	Fe
302/83dr	L.R. 4-5 c	Fragment of a buckle -drilling	86.70	.10	6.50	6.70	Fe
303/83	L.Roman	Bronze plate - surface	73.00	9.00	7.00	10.00	Fe
303/83dr	L.Roman	Bronze plate - drilling	74.30	4.50	8.30	10.50	Fe
304/83	L.Roman	Piece of a mirror (?) -surface	70.00	18.00	7.00	4.00	Fe
304/83dr	L.Roman	Piece of a mirror - drilling	78.90	6.70	10.90	1.60	Fe
320/83	L.R. 3c AD	Axe pendant - surface	60.00	.10	30.00	7.00	Fe
320/83dr	L.R. 3c AD	Axe pendant - drilling	80.40	.10	17.40	1.70	Fe
3541/77	L.R. 3c AD	Molten lump of golden metal	71.67	14.00	.50	13.76	nd
3542/77	L.R. 3c AD	Silver fibulae	46.00	.10	2.00	.80	Ag 51%
3543/77/a	L.R. 3c AD	Fragments of bronze	88.41	10.87	.10	.72	nd
3543/77/ad	L.R. 3c AD	Fragments of bronze	86.00	12.70	.10	1.30	Fe
369/83	L.Roman	Piece of metal - surface	70.00	.10	30.00	.10	nd
369/83dr	L.Roman	Piece of metal - drilling	64.80	.10	35.10	.10	Fe
380/83	E.R. 1c AD	Roman fibulae, tin plated-surf	77.00	9.50	10.00	3.00	Fe
380/83dr	E.R. 1c AD	Roman fibulae, tin plated-dril	77.10	3.90	15.70	2.90	Fe
469/84a	L.R. 2-3 c	Bronze fibulae:body	90.00	5.00	.10	5.00	Fe
469/84b	L.R. 2-3 c	Bronze fibulae:decoration	90.00	3.00	4.00	3.00	Fe
47/82	L.Roman?	Corroded bronze - surface	81.00	.10	12.00	3.00	Fe
47/82dr	L.Roman?	Corroded bronze - drilling	72.90	.10	23.80	2.80	Fe
511/84	L.R.3-4c	Bronze fibulae	96.00	2.00	2.00	.20	Fe
515/84	L.Roman?	Bronze sheet - surface	84.00	1.00	8.00	5.50	Fe
515/84dr	L.Roman?	Bronze sheet - drilling	90.70	.32	5.80	2.30	Fe
568/84	L.Roman?	Bronze fragment - surface	72.00	1.00	20.00	5.00	Fe
568/84dr	L.Roman?	Bronze fragment - drilling	78.70	6.30	10.40	4.40	Fe
86/82	L.Roman	Bronze fragment	97.00	.10	1.50	.50	As 0.5%
95/82	L.Roman	Bronze disc - surface	80.00	5.00	.10	15.00	nd
95/82dr	L.Roman	Bronze disc - drilling	60.00	5.90	4.00	30.10	nd
97/82	L.Roman	Needle - surface	65.00	19.00	14.00	2.00	Fe
97/82dr	L.Roman	Needle - drilling	66.50	11.80	17.50	2.00	Fe
989/86	L.R. 3c AD	Axe pendant	90.05	.10	7.30	1.91	Fe

must be regarded as entirely impractical.

The XRF analyses of metal finds from Jakuszowice and Opatow show that the alloys are made of copper, zinc, tin and lead mixed in varied and very inconsistent proportions. Figure 39 presents a bar-chart of the major compositions of drilled samples from small 'bronze' finds from Jakuszowice and Opatow.

The amount of zinc and lead in the alloys ranges from 0-36% and similar variations are observed for tin. There seems to be no group of objects of a uniform composition; almost every object is different. It is rather surprising that not a single artefact from the workshop in Jakuszowice proved to be of unleaded tin bronze (Cu/Sn), which was the most common Bronze Age Mediterranean metal and is quite frequent also in Roman times. There are, however, two fragments from the grave in Opatow which are made of tin bronze with only about 1% of lead. The most common type of alloy amongst the metals from Jakuszowice is a ternary Cu/Zn/Pb alloy which forms nearly half of the analysed material. The other two large groups of alloys are Cu/Sn/Pb and Cu/Zn/Sn/Pb. Lead and zinc are far more common in the alloys than tin.

Lead in concentrations above 1% was found in 81% of analysed copper-based objects and many lead pieces were also found on the site. It is interesting to notice that not all of the lead is in fact chemically pure: three of the pieces contain varying quantities of tin (Nos. 1390, 1886 and 229 in Table 11), and three have traces of copper (Nos. 1197, 1390 and 1778). The amount of copper is very low and might be accidental, but in all three cases tin must have been deliberately added to lead. The Greek and Roman tin-lead solders were made in the proportions 2:1 for fine work, 1:1 for common solder, and 1:2 for plumber's solder (Healy 1978, p. 239). The tin-to-lead ratios in the three pieces from Jakuszowice (Nos. 1390, 1886 and 229) are 1:4, 1:49 and nearly 1:7 respectively. This very low tin content seems to emphasize again the shortage of tin in Jakuszowice, but equally might be a result of random trials of making a Roman-style

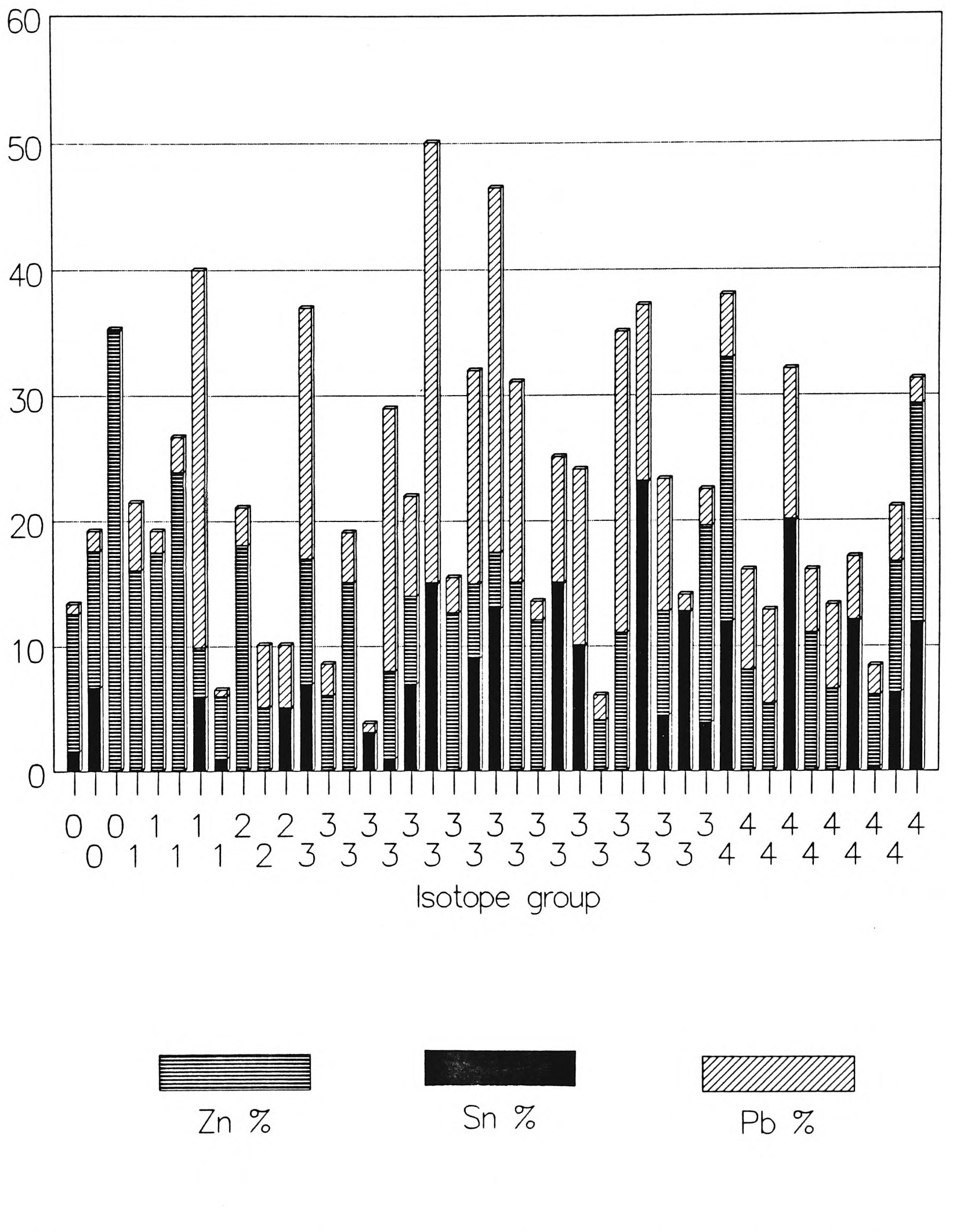


Fig. 39. Bar-chart of the alloy compositions of copper-based metals from Southern Poland. Numbers from 0 to 4 indicate different lead isotope groups.

solder. The comparative abundance of lead amongst other non-ferrous metals on this site is particularly interesting, because Jakuszowice is less than 100 km away from the large lead-zinc deposits of the Silesian Olkusz district. The mines in Olkusz were well known in the Middle Ages for their silver production. However, nothing is known about the exploitation of the minerals in Olkusz before Mediaeval times. It seems not impossible that lead (and perhaps also silver) from Olkusz was exploited much earlier. It is tempting to presume that this, comparatively large, amount of lead in Jakuszowice is there due to the use of lead from Olkusz in the preparation of the alloys from imported copper-based metal. Only five analysed objects show lead content below 1% (Nos. 1822, 3543a, 369, 511, 86). No. 3543 is a molten lump of golden metal from the grave in Opatow mentioned above, and 369 is a triangular fragment of a high-zinc brass sheet, possibly raw material for making alloys. No. 1822 is a bent and broken needle and 86 is another half-finished one. The lead content in 30 out of 49 metals is below 5%. Nieweglowski (1986, 317) concluded that the Cu/Zn/Pb alloy has the best quality, both for casting and hammering, when zinc content is below 20% and lead about 3% or less. Figure 40 shows the lead and zinc content in the copper based objects from Poland. Only three objects have more than 20% of zinc and 2 of them have also some lead. The amount of lead associated with other objects containing also zinc is widely varied. The scatter plots of zinc, lead and tin in all copper based artefacts from Jakuszowice and Opatow show no correlation between these three metals.

The results of alloy analyses of these metals are very interesting from the point of view of the possible sources of metals. If one could compare their composition with metals from the Roman Empire, than perhaps it would be possible to see the resemblance, or difference, between the alloy types in those two groups. It must be mentioned here that the suggestion of the use of Roman coins as the source of raw material seems rather unlikely in the view of the great

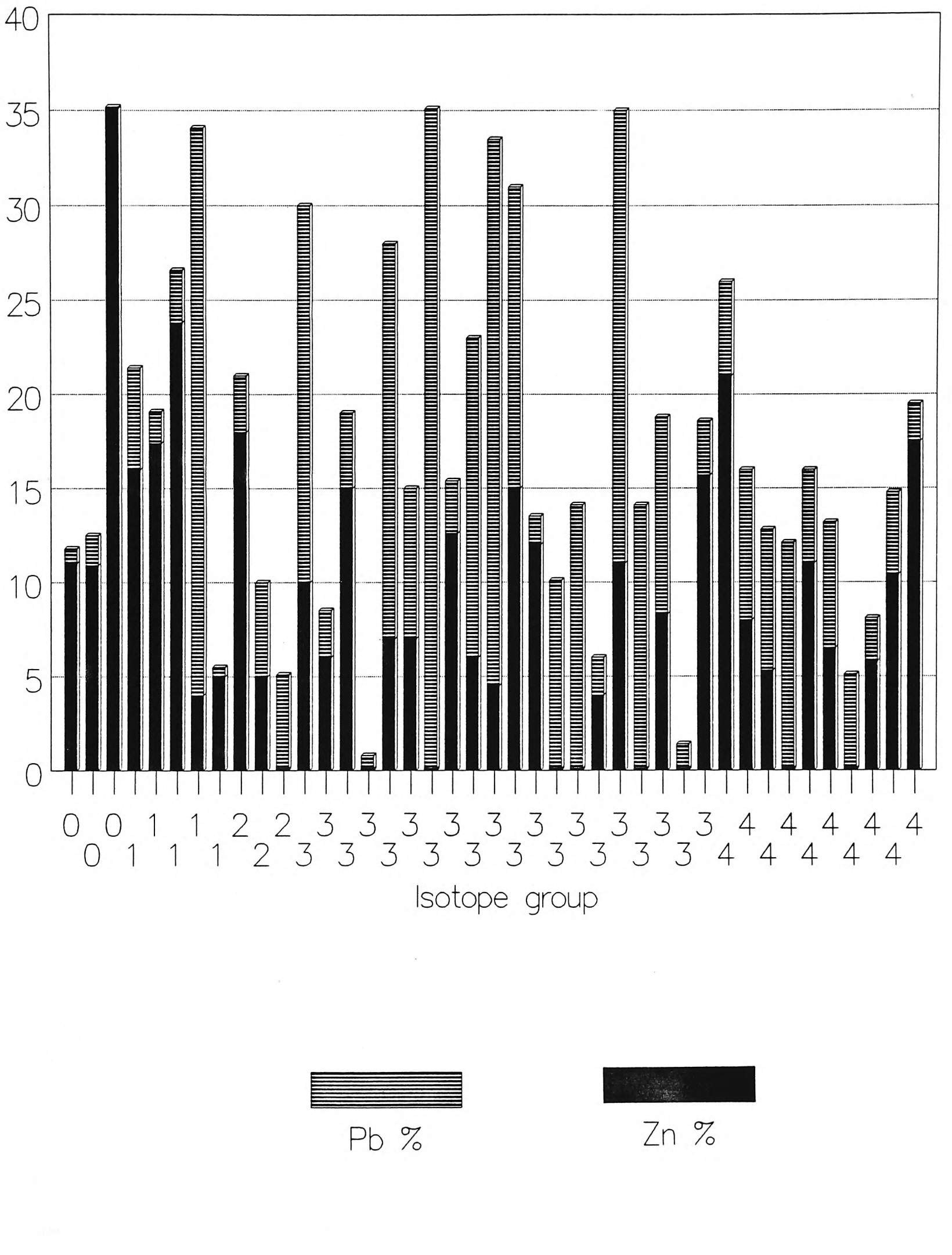


Fig. 40. Lead and zinc content in the copper-based alloys from Poland.

variety of metal contents in the artefacts from the metal workshop at Jakuszowice. Numerous analyses of Roman coins show that their alloy compositions were quite well controlled, and melting them together should produce a standard alloy. Two recent publications give results of a large number of objects dated to the first centuries of our era from France and from Britain (Beck et al. 1985 and Mortimer et al. 1986). The British copper-based alloys are some 100 to 200 years later than the Polish assembly, but the type of alloys resembles them closely and the authors suggest that the metal might have been made from Roman scrap. However, all of the British metals contain tin and the quantities of all three metals (zinc, tin and lead) are strongly correlated. The tin-lead content correlation led the authors to postulate that Roman pewter, which was made of tin and lead in proportions 2.5:1, was added to the alloy. Such correlation does not exist amongst the Polish metals and tin is present only in less than half of them; therefore it seems that they cannot have been made from metals of this type. Oddy and Craddock (1983) remark that in Roman brass generally tin correlates negatively with zinc. There is no such correlation amongst the Polish metals either.

The analyses of two groups of Gallo-Roman artefacts mentioned earlier provide at present the best comparison for the metals from Jakuszowice. They include many objects and a wide cross-section of types of metals and artefacts. In a preliminary way they can be treated as a typical assembly of metals from a provincial Roman metal production for local use and for trade. The results of chemical analyses of the Gallo-Roman "bronzes" resemble quite well the compositions of Polish metals (Beck et al. 1985 and Rabeisen and Menu 1985). The French bronzes cover about 5 centuries between 1c. BC and 4c. AD, but the great majority dates to 2nd and 3rd century AD. The Polish metals are dated also between 1st and 4th century AD. The main group of Gallo-Roman bronzes includes analyses of samples of 417 objects from various museums in France (by

ultraviolet emission spectrometry); they are mostly statues, figurines, small ornaments and vessels. Such objects could have been imported into *Barbaricum* and used as scrap, but perhaps more justified is the comparison of the metals from the workshop in Jakuszowice with the analyses of the material from the bronze workshop in one Gallo-Roman village of Alesia which prospered between 1st and 4th century (Rabeisen and Menu 1985). The metal supplies of this village certainly included 'fresh' copper, because a number of pure copper ingots was excavated there, as well as 'raw' tin-bronze in the shape of Cu/Sn rings. The metallurgical remains include scrap metal and remains of metal in casting moulds. An assembly of artefacts which might have been made there, or used as scrap metal, consists of small ornaments, some vessels and statues. Also one piece of lead was found on the site. The authors give chemical analyses of 94 copper based objects of very different compositions.

A scatter-plot comparison of the chemical compositions of the metals from Alesia and Poland (Figure 41) does not show a striking difference between the type of alloys used on both sites. There are no significant correlations between the three metals added to copper, and the alloy compositions of metals from Alesia are nearly as varied as the Polish artefacts. There is, however, a difference between these two groups in the much smaller proportion of tin and larger variation in the content of lead, zinc and tin in the Polish metals. Table 12 shows the mean values and standard deviations of the concentrations of tin, zinc and lead in both groups of metals (the pure copper ingots from Alesia were omitted from these calculations).

It is most interesting that the mean values of metals present in these two incidental groups of from the same period, one from the Roman Gaul, and the other from the *Barbaricum* show such similarity. The standard deviations of the Polish group are higher, which confirms the larger quantitative range of alloy compositions mentioned earlier. The general chemical compositions of the

Table 12. Mean values of tin (A), zinc (B) and lead (C) in copper-based metals from Jakuszowice and Alesia.

MEANS

GROUP = VARIABLE	ALESIA	POLAND	ALL GPS.
1 A	3.24864	3.65729	3.40070
2 B	9.56296	9.89729	9.68736
3 C	6.21986	6.59458	6.35930
COUNTS	81.	48.	129.

STANDARD DEVIATIONS

GROUP = VARIABLE	ALESIA	POLAND	ALL GPS.
1 A	2.84564	5.22058	3.89708
2 B	7.50746	8.09730	7.73099
3 C	6.83523	7.85957	7.23125

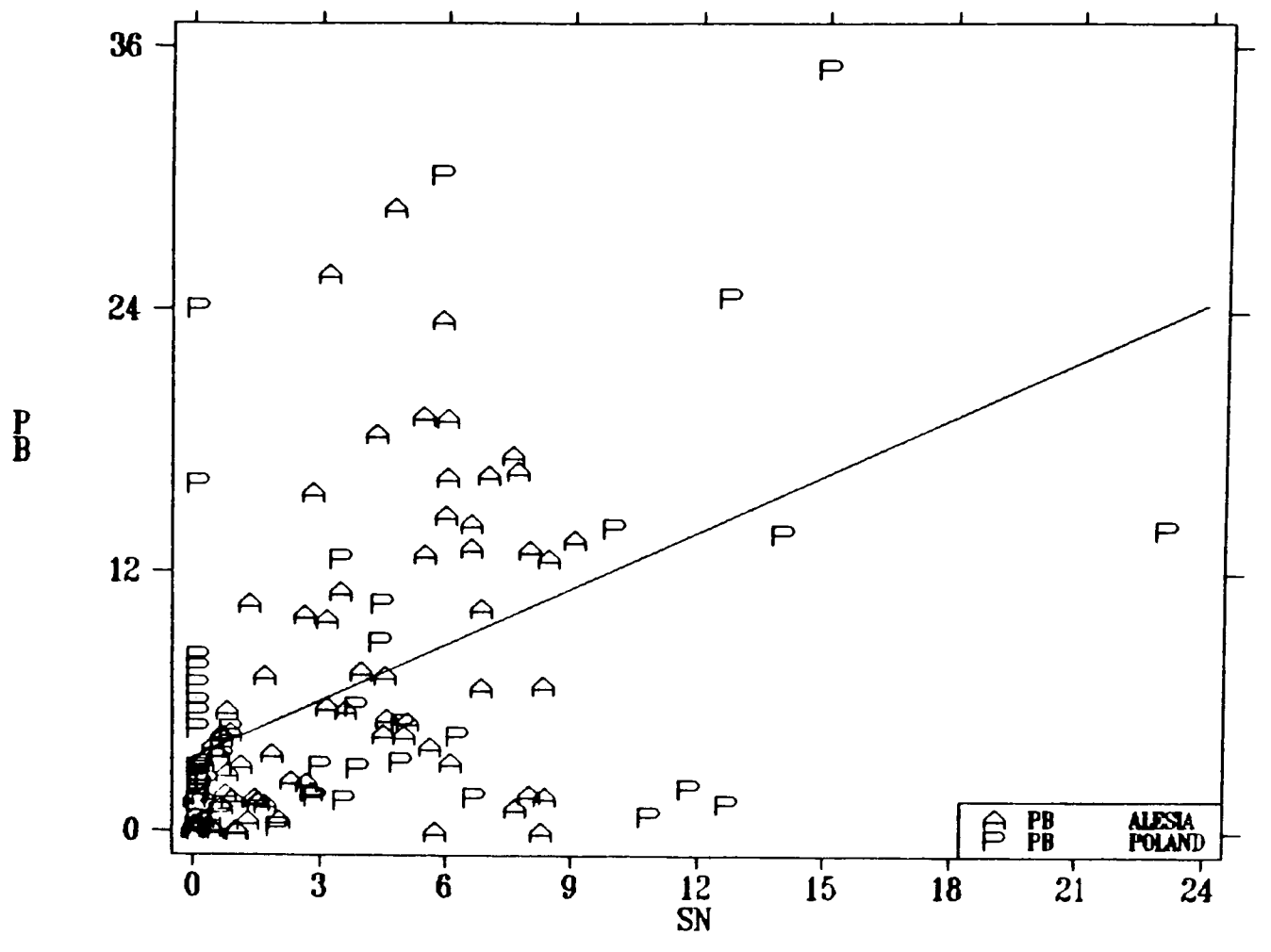
Gallo-Roman bronzes and Polish bronzes are quite similar, but the proportions of alloy types in each of the groups is different. Table 13 shows the comparison of metal types found in the Polish group and two groups of the Gallo-Roman bronzes.

Table 13. Comparison of metal types of Polish and Gallo-Roman copper-based alloys.

Group	% of Polish	% of Gallo-Roman	% of Alesia
Alloy Cu/Zn	2.00	2.00	35.00
Alloy Cu/Zn/Pb	47.00	2.00	17.00
Alloy Cu/Sn	0.00	7.00	7.00
Alloy Cu/Sn/Pb	20.00	52.00	30.00
Alloy Cu/Pb	2.00	.50	0.00
Alloy Cu/Pb/Sn/Zn	24.00	36.00	11.00
Alloy Cu/Sn/Zn	2.00	.50	0.00
Tin in bronzes	45.00	88.00	62.00
Zinc in bronzes	75.00	63.00	61.00
Lead in bronzes	81.00	73.00	68.00

There is a striking difference in the proportion of copper-zinc-lead (Cu-Zn-Pb) alloys amongst the French and Polish metals. In the Polish group this alloy composition was found in 47% of the total of objects, compared to only 2% for the Gallo-Roman and 17% of Alesia. In Alesia brass (Cu-Zn) objects form 35% of the total metal finds. Amongst the analysed objects from Jakuszowice there is only one small metal fragment which is made of brass (No. 369/83). Not a single pure copper or bronze (Cu-Sn) object was identified amongst the Polish finds, but 7% of the French metal is unleaded tin bronze. It seems that tin was more of a rarity in southern Poland than in France: tin was found in 88% of the Gallo-Roman bronzes, whilst only in 45% of the Polish metals, but the picture might be somewhat distorted by the large number of large statues amongst the Gallo-Roman 'bronzes'. Tin in metals from Alesia occurs in a very similar proportion of the analysed alloys to that of the Polish group (48%). On the other hand, zinc is more frequent amongst the Polish finds; there is even one curious piece of metal containing 95% of zinc and 5% of lead. One wonders if this could be an accidental result of zinc condensation on the walls of the furnace during smelting of either lead or copper from zinc-rich mixed ores. The amount of bronzes with added lead is highest amongst the Gallo-Roman bronzes (90.5%), but again the statues might have influenced the result, because lead is known to be always added to large cast objects. Lead appears in a much larger proportion of Polish alloys, though, when compared with metals from Alesia (81% as opposed to 58%). Also much more lead scrap was found in Jakuszowice than in Alesia.

The comparison of lead and zinc contents in the metals from Jakuszowice and Alesia (Fig. 41 b) does not show much difference between them, beyond the overall larger percentage of Polish samples containing lead. If the Polish metal artefacts were made from recycled metal, than their zinc content should be lower than in the 'fresh' metal from Alesia, because zinc is very volatile. This



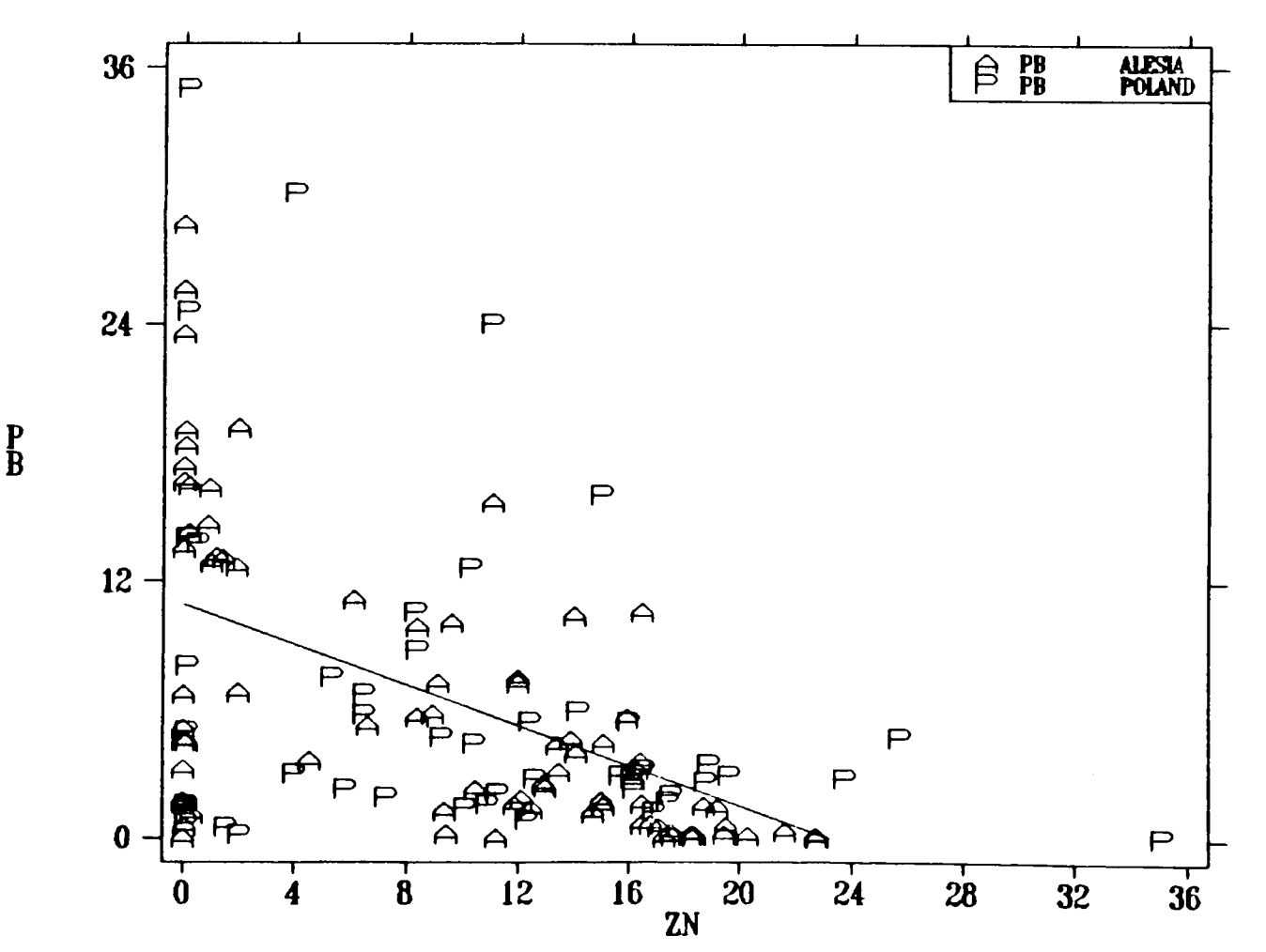


Fig. 41. Scatter-plots of the tin, lead and zinc concentrations in the metals from Jakuszowice and Opatow, and Alesia. a) comparison of lead and tin, b) comparison of lead and zinc concentrations.

feature is definitely not represented here. Not only on the scatter plot does the majority of Polish alloys fall squarely into the same region as the metals from Alesia, but also they show a slightly higher mean zinc concentration (9.89%) than the French metals (9.56% and 9.68%). It is also worth mentioning here that in all Polish metals iron was detected in concentrations of tenths of a per cent, or higher. The iron content is known to fall during remelting, so it seems that if the metals from Jakuszowice were made from scrap, then it must have been a comparatively 'new' one which was not repeatedly recycled.

Nevertheless, in view of the chemical composition of metals from Roman Gaul and the Polish sites, the archaeological theory of re-using metals from the Roman Empire in *Barbaricum* cannot be readily rejected. On the other hand the similarity and certain uniformity of the metallurgical technology across Europe in the first centuries of our era is likewise quite possible, and the fact that metals from distant sites have similar alloy compositions does not necessary prove that they have a common origin. Already in the Bronze Age similar metal production technologies were carried out throughout Europe and in the pre-Roman times the Celts, who occupied lands reaching nearly to the present day Polish borders, had highly developed metallurgy. Unfortunately, there are no certain Celtic non-ferrous mines and slag heaps in Central Europe, and on the whole very little is known about the prehistoric metal sources in this part of the world. It seems that lead isotope analyses of the metals are essential here to bring another dimension to the discussion.

8.4. Comparison of the lead isotope compositions of Gallo-Roman bronzes and the European ore deposits.

The possibility of extensive use of scrap metal originating from different regions and characterized by different lead isotope signatures has always been emphasized as the greatest possible limitation of lead isotope provenance studies. The main weight of the argument is in the fact that the process of remelting

and mixing of several objects, made of metal of different origin, will change the original lead isotope signatures coming from the ore deposits. The final lead isotope composition of an artefact made of scraps of metal originating from many different sources will be totally unpredictable, because above all it depends on the quantity of lead in each piece of metal and the portion of this particular metal in the finished alloy (the composition will of course lie within the isotopic ranges of all the components). The Roman 'bronzes' present quite a new challenge to the lead isotope provenance studies, because much has been said of the Roman trade in metals within and outside the empire. If indeed many sources of copper were used in each part of the Roman Empire, and then the metals were exported and scrap melted together, then we would expect a wide variety of lead isotope compositions of the Roman metals from one site. Theoretically one can expect any composition on the straight line joining the lead isotope fingerprints of the original ore deposits. There is a considerable probability that at least some artefacts should retain the original composition. It is very important therefore to know as well as possible the lead isotope characteristics of the European ore deposits which might have been exploited by Romans.

The number of such ore deposits in Europe is not unlimited and the transport of large quantities of metal across continental Europe must have been rather slow. It therefore seems possible that people in certain areas were in fact predominantly using quantities of non-ferrous metals exploited in the nearest regions, and therefore most of their alloys were made from metal of the same origin. Such economically satisfactory connections might have been established even before the Roman conquest. Very little is known for example about the Celtic mines, which must have existed in Western and central Europe to supply the large amount of bronze used by the Celts. It is not unlikely that the Celtic metallurgical traditions were continued during the Roman times and there was no need for the Roman-Gauls, for example, to import much metal from other

parts of the Empire.

Not all the provinces of France have their own economically important deposits of non-ferrous metals (see Figure 12). However, in Southern France, in the mountains of the Massif Central, copper, lead and zinc minerals are in a quantity which would be economically valuable in the Roman times (Ridge 1990). Further east there are the ore deposits of Schwarzwald, Austria and the Rhine. To the south there are deposits, certainly exploited in Roman times, in Spain, on Sardinia and Elbe and on the Italian Mainland.

The lead isotope analyses of 56 Gallo-Roman bronzes (Beck et al. 1985) show a core group of 48 bronzes with the range of values for their lead isotope ratios of 2.073-2.097, 0.844-0.854 and 18.2-18.56. The percent range of all three lead isotope ratios is a little above 1%. According to the estimates of the average lead isotope percent range within one ore deposit (see Chapter 6), this figure fits well with the measured ranges of some of the comparatively small geographical areas, covering several deposits displaying slightly different lead isotope characteristics. For example, Cyprus and the Othrys Mountains show a similar range of lead isotope compositions. It is important to notice, that there are no samples of higher 208/206 ratios, so there is no indication that the 'core group' was made from mixing metal of higher and lower lead isotope ratios (Figure 42). The grouping does not suggest that the metals originated from a great variety of sources, because the great majority of lead isotope signatures of these Gallo-Roman 'bronzes' falls into a comparatively small and compact isotopic space 'globule'. Only a few objects are made of metal of quite different origin (those have lower 208/206 lead isotope ratios). A closer consideration of the objects falling outside the main group (imports maybe?) shows that two of them are consistent with the lead isotope ratios of the Lavrion ores and lead and litharge from two Classical lead/silver smelting sites in this area: Thorikos and Agrileza (Nos. 6212 and 1918, not plotted on Figure 42, because they are beyond the

range of lead isotope ratios shown on this diagram). Only one of these objects can be found in the list of chemical analyses (6212 - Beck et al. 1985, p.122) and it is made from leaded tin bronze (Zn less than 0.001%). This alloy composition is quite consistent with the typical metals used in Greece (Craddock 1976) and perhaps the statue, or its metal, is an import from Greece. In theory the five objects scattered on Figure 42 between the 'core group' and the 207/206 ratio of 0.8373 could have been made of a mixture of the metal from the 'core group' and, for example, Lavrion. However, there are also other European ore deposits which have copper/lead/zinc ores, and their lead isotope compositions fall in the same region of the diagram.

The authors of the report on Gallo-Roman bronzes used their lead isotope analyses to characterize different workshops and concluded that: "Il ressort des analyses que les cinq groupes geographiques peuvent etre differencies par leurs teneurs isotopiques. ... Au-dela du centralisme, des refontes frequentes et attestees, il semble donc subsister une specificite regionale du metal et une utilisation par les metallurgistes des mines locales." A more careful examination of the data shows that the differences between regions are not absolutely clear cut (Beck et al. 1985, p.110-111, figs. 7 and 8), but definitely there is a general tendency for the majority of objects from one area to fall closely together. It might be significant, for example, that on our diagram of the data (Figure 42) the majority of objects from the Bavai-Narbonensis plot in the upper part of the "core group", whilst the isotopic compositions of metals from Alsace-Aquitaine workshops fall predominantly into its lower part. The authors of the report do not suggest any specific mining districts which would be regarded as 'local'.

The geological literature (Ridge 1990) suggests that the multimetallic mines of Massif Central, which for certain have been exploited in ancient times, are in the region of Malines. It might seem too obvious an answer, but lead isotope data for this deposit published by Brevart et al. (1982) fall squarely

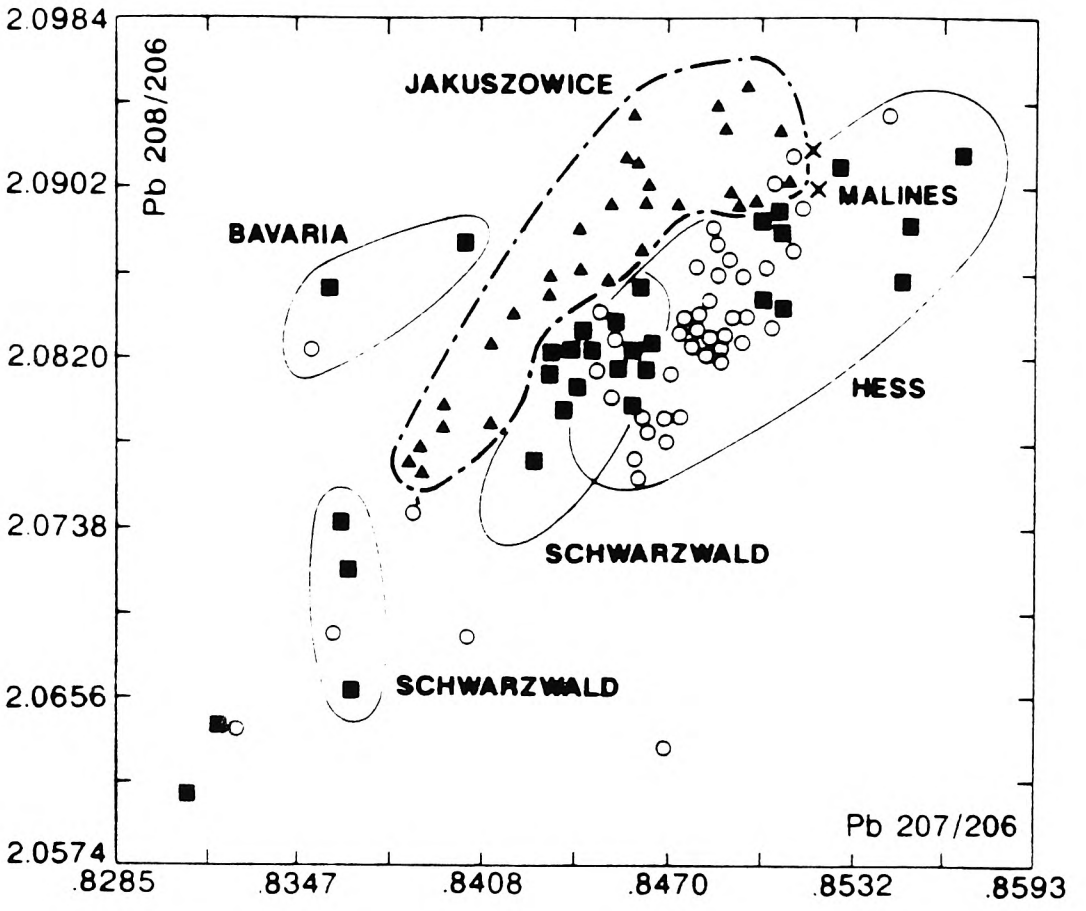


Fig. 42. Comparison of lead isotope compositions of Gallo-Roman 'bronzes', Polish metals and matching European ores.

into the upper part of the Gallo-Roman data plotted on Figure 42 (for the lead isotope data of Gallo-Roman bronzes compared with Malines and other French ore deposits see Appendix 3). However, no other published lead isotope data for the Massif Central, or another French copper/lead/zinc, or only lead, deposit, is consistent with the isotopically lower part of the Gallo-Roman bronzes. On the other hand, not so far east from the provinces of Aquitaine and Alsace, along the upper Rhine, there were Roman forts guarding the production of silver (of which lead is a by-product) and also there are considerable deposits of other metals. A few years ago we made a number of lead isotope analyses of the minerals from the area of the Roman fort in Heftrich and from the Kaisergrube lead/silver mine in the Taunus Mountains (Zwicker et al. 1986), where Roman mining was attested by Kobrich (1936, 36). The lead isotope ratios of these Rhine-centred deposits agree well with the Alsace-Aquitaine group of the Gallo-Roman bronzes. A further two bronzes, falling outside the main isotopic group (one from Aquitaine and one from Alsace), are consistent with their origin from the mineralization near Teufelsgrund in Schwarzwald. No other presently available lead isotope data for the European ore deposits (including Spain, Italy, Greece and Britain) are consistent with the compositions of the Gallo-Roman copper-based metals.

This interpretation of the lead isotope data of the Gallo-Roman bronzes is very preliminary. The lead isotope and archaeometallurgical evidence for the French and Austrian deposits is particularly poor in comparison with the comparative data base for the Mediterranean. There is **much more** analytical and geological field work needed in these parts of Europe to unravel the secrets of the Roman production and trade in metals. However, even at the present stage the archaeological and geological lead isotope data seem to be telling us a very likely story and forms an important spring-board for further research.

8.5. Lead isotope analyses of the Polish metals from the Roman period.

The lead isotope analyses of metals from Jakuszowice are interesting from several points of view; some of them have been highlighted in the previous chapters. The identification of metals imported from Western or Southern Europe amongst the objects from Jakuszowice would greatly strengthen the archaeological hypotheses in regard to the trade links, and provide the first scientific evidence of metal trade between the Empire and *Barbaricum*. The results of analyses are also interesting from the point of view of applicability of lead isotope technique to alloys, many of them containing lead in high proportion, from an archaeological context where many different and distant sources of metals might have been used. A further interest is in the examination of the hypothesis that some of the local minerals were exploited.

Fifty-nine small metal objects from Jakuszowice were sampled for lead isotope analyses. In this number there were forty-three 'bronzes', four silver and twelve samples of lead; mostly scrap. The complete objects included fibulae, needles, and some small pendants. Four samples of metal were also taken from the Chieftain's Burial from Opatow (Nos. 1143, 3541, 3542, 3543; the silver fibulae 3542 was sampled in Krakow and there is no photograph.) The silver brooches are well preserved, but the other three samples from Opatow are shapeless lumps of molten metal. Following the hypothesis of the import of metals from the Roman Empire to *Barbaricum*, the comparison of lead isotope compositions of the Gallo-Roman metals with the Polish group might show if any of the same sources were used in both regions. If indeed the Rhine deposits, Schwarzwald and Massif Central mines were exploited in the Roman times, and the metal used in the Empire was re-cycled in *Barbaricum*, then perhaps the lead isotope signatures of these deposits should be reflected at least in some of the metals from the Polish sites. Alternatively, the lead isotope compositions

of Polish metals can be compared with the whole range of the Mediterranean, Polish, British, Bulgarian and Austrian copper and lead ores, as well as with the published data for the Bohemian Massif and Harz (the lead isotope ore data are in Appendix 3).

Lead isotope analyses of the metals from Jakuszowice and Opatow are listed in Table 16 and plotted on Figure 43. The first striking feature of these data is the fact that nearly all lead pieces group tightly together and away from the copper-based alloys! This is a great surprise, because it seems certain therefore, that not only has the lead found on the site not been added to the copper alloys, but also that all these pieces of lead originate from a mineral deposit different from all the sources of lead in the copper based alloys and silver. The comparison of the lead isotope ratios of the lead metal from Jakuszowice with those of the lead ore deposits shows a high probability that its origin is the Silesian mines in the Olkusz district. It has been mentioned earlier that there is no other evidence for exploitation of metals from this mineralisation during the Roman times. However, the lead metal samples cluster together very tightly and there is no silver or 'bronze' matching their lead isotope composition. The mean values of all three lead isotope ratios for the group of galenas from Olkusz and lead from Jakuszowice are within the limits of one standard deviation (Table 14). The stepwise discriminant analysis shows high posterior probabilities for the Jakuszowice group of lead artefacts belonging to the group Olkusz.

The lead/silver/zinc deposits of Silesia are very large in European terms and have been exploited extensively since the Middle Ages. Copper, lead and zinc minerals are also present there in large quantities and may have been exploited (Osika 1986, 55, 69-77). In recent times Olkusz has been particularly well known for its lead and zinc production. It is estimated that up to the middle of the present century, 16×10^6 tonne of zinc and 4×10^6 of lead metal were produced from the ore. At present, the area looks like a horribly polluted

Table 14. Mean values and standard deviations of lead isotope compositions of lead from Jakuszowice and galenas from Olkusz. A, B and C are the lead isotope ratios 208/206, 207/206 and 206/204 respectively.

NUMBER OF CASES READ. 22

MEANS

GROUP =	OLKUSZ	JAKUSZOW	ALL GPS.
VARIABLE			
1 A	2.08763	2.08575	2.08678
2 B	0.84842	0.84809	0.84827
3 C	18.45550	18.42670	18.44241
COUNTS	12.	10.	22.

STANDARD DEVIATIONS

GROUP =	OLKUSZ	JAKUSZOW	ALL GPS.
VARIABLE			
1 A	0.00155	0.00182	0.00168
2 B	0.00028	0.00048	0.00038
3 C	0.02482	0.01868	0.02227

moon-scape, with vast sandy deserts. Many mines are still in operation and there is not much hope of finding any traces of Roman exploitation. Twelve samples of galena included in this study originate from the mines near the small town of Olkusz, but there are many such mines stretching away to the west and south, and it is possible that the lead isotope 'fingerprint' of Olkusz might overlap with some of the other mineralisations. At present, however, the description 'Olkusz' seems most suitable in this preliminary part of the research. It is very interesting to see that lead metal from Jakuszowice is so distinctly different in its origin from the copper-based and silver alloys. Perhaps the people working with metals in Jakuszowice did not realise that the golden, reddish and silvery metals contain the humble, grey lead. It seems probable that each of the metals of different colours was treated as a separate material. If the craftsmen from Jakuszowice were experimenting with melting together metals of different

appearance, then lead was not included in this process.

I have also analysed at Oxford (using the ED XRF method) several fragments of crucibles from Jakuszowice. The red and black slag-glaze inside the shards contained copper and zinc, but very little lead. The elemental analyses of slags on the crucibles do not show any evidence that they might have been used for melting lead. Another aspect of non-ferrous metallurgy which does not seem to have been carried out in southern Poland at that time is the cupellation of silver. Since the mines of Olkusz were known several centuries later as the most important Polish silver mines, it is rather surprising that together with lead there is no silver from Olkusz in Jakuszowice.

Table 15. Posterior probabilities of the origin of lead from Jakuszowice from the Silesian lead/silver/zinc deposit of Olkusz (column 'OLKUSZ').

CASE	GROUP JAKUSZOW	OLKUSZ	JAKUSZOW
13		2.3 0.270	0.0 0.730
14		2.3 0.248	0.0 0.752
15		3.8 0.156	0.4 0.844
16	OLKUSZ	0.2 0.809	3.1 0.191
17		0.5 0.470	0.3 0.530
18	OLKUSZ	0.1 0.585	0.8 0.415
19		2.3 0.248	0.0 0.752
20		2.7 0.217	0.1 0.783
21		4.2 0.141	0.6 0.859
22		4.9 0.115	0.9 0.885

The silver and 'bronzes' from Jakuszowice and Opatow fall into a quite different and much wider range of lead isotope ratios than the lead metal (208/206 is from 2.075 to 2.097). However, in parallel with the Gallo-Roman bronzes, they do not reflect a great geological variety of origin. The range of 208/206 lead isotope ratios is only 1.2%. And again, there is a large 'core group', with only a few artefacts tailing at the lower end of the 208/206 versus 207/206 diagram. The

silver fibulae and discs have lead isotope ratios largely indistinguishable from the copper-based metals. However, the lead isotope data of the Polish metals do not fall into the same part of the lead isotope diagram as the Gallo-Roman bronzes and the ores from Massif Central and Rhineland. In the isotope diagram the whole group is shifted above the group of the metals from France. The 'core group' includes nearly 40 artefacts of very varied alloy compositions. Figure 40 shows a bar chart of the alloy composition of the artefacts in order of their lead isotope ratios. Clearly, there is no connection between the lead, zinc and tin content and the lead isotope compositions. Such mixed alloy compositions within a small lead isotope range (possibly of one mineral deposit), and particularly the fact that in each of the isotope groups there are artefacts with very high and very low lead content (below 1%), suggest that the alloys might have been made originally in the areas where multimetallic ores were mined and smelted. The production of brass by cementation certainly could have been carried out in the most efficient way in places where the supplies of calamine and copper metal were available at hand. Lead might have been added separately as metal, or might have been already in the copper. On the whole the similarity of the pattern of lead isotope compositions of the Polish metals to the Gallo-Roman bronzes is rather striking. One could say that even if the geographical sources of metals for the Gallo-Romans and the 'Barbarians' were not identical, the types of metal and the technology of making them must have been pretty similar.

There are three metal fragments from the group of metals from Jakuszowice which are isotopically distinctly different from the rest of the artefacts (and from any of the Gallo- Roman metals). One of them, a fragment of a mirror (304/83), has a lead isotope composition quite unique amongst all other metals discussed here and not known amongst the European ore deposits. The very high 208/206 ratio of 2.177 indicates that the geological age of the ore deposit used for production of this high tin bronze is more than 700 million years. Lead

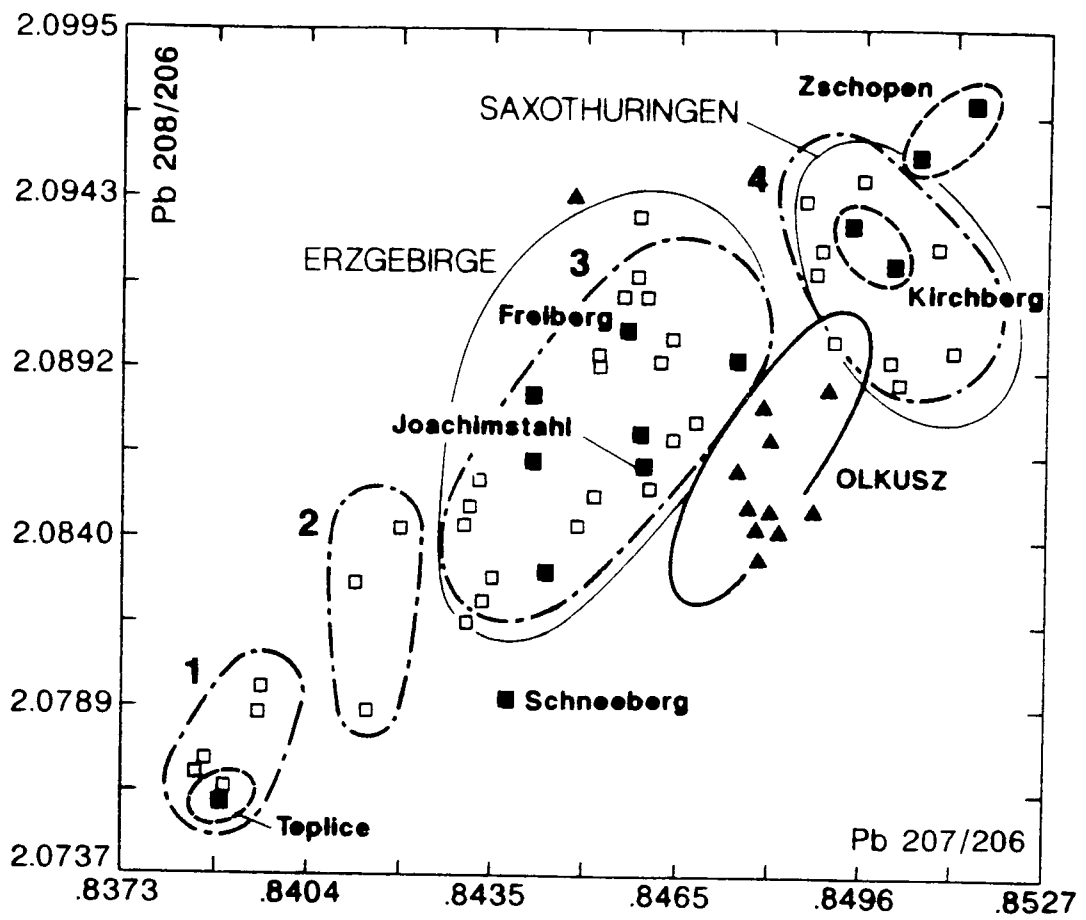


Fig. 43. Lead isotope compositions of metals from Jakuszowice and Opatow (black triangles - lead, open squares - copper and silver alloys) and isotopically matching ores (black squares).

isotope compositions in this range have been measured in our laboratory only for the minerals of the Iranian Plateau. However, an exact match has not been found amongst the data on our database and at present its geographical origin remains unknown. It seems most likely, though, that this fragment of metal is of a non-European origin. The other two metal fragments, a needle (1822/88) and the only piece of real brass (Cu/Zn alloy) have different lead isotope compositions, but in both cases they are consistent with the lead isotope signatures of the rich lead-silver-zinc-copper deposits of the Iglesias district in South-West Sardinia. The needle matches the lead isotope composition of the ores from Sa Marchesa and the piece of brass that the mines of Perda s'Oliu (Stos-Gale and Gale 1992). The lead content of both pieces is below 0.5%, which indicates that the metals were made by metallurgists of experience. Pliny (Natural History XXXIII-XXXIV) mentions Campania as the centre of the Roman brass industry. The main centers of this activity were in Puteoli, Nola and Capua. All these three sites are situated on the Italian Mainland just beyond the island of Ischia, directly opposite the island of Sardinia. Healy (1978, 61) mentions that the "lead works in Puteoli relied on imported ore", and that the mines near Iglesias were exploited by the Romans. It is probable that the metals used in Campanian production centers were imported from several mining districts. However, the closest plentiful sources of zinc and lead minerals are on Sardinia. Tuscany is famous in the archaeological literature as the Etruscan copper source; it is not impossible that some copper from Tuscany might have been used in Roman Campania for the production of brass. The Tuscan deposits, however, have only some lead ores and practically no zinc. Iron and copper are most likely to be the main metals made from the Tuscan ores; for lead, silver and zinc Sardinia has no equal in this part of the Mediterranean.

Figure 43 shows the plot of the lead isotope ratios of the majority of metals from Jakuszowice and Opatow, including the four silver artefacts. Four objects

from Opatow have lead isotope compositions falling with the metals from Jakuszowice, and most probably were imported from the same source as Jakuszowice; therefore all objects are plotted together on the diagram. The search for matching lead isotope 'fingerprints' through our lead isotope database of nearly 1500 data from over 100 ore deposits shows that they are distinctly different from all the known multimetallic deposits in the Mediterranean and Western Europe (including Britain). On the other hand, a near-perfect match for the majority of these artefacts is found amongst the ores from the region of Erzgebirge (Saxony-Bochemia border) published by Bielicki and Tischendorf (1991).

The geochronology of the mineral deposits in Central Europe is very complex. I was able to collect nearly 300 lead isotope data for mineral deposits in Poland, Germany, Bohemia, Austria and Switzerland. Most of the data were published in the geological periodicals, and only occasionally more than one or two samples for one deposit have been analysed. However, even this limited number of lead isotope data shows a quite considerable variety of lead isotope compositions and the great majority of them are not consistent with the metals from Jakuszowice. It is greatly encouraging that those lead isotope analyses which are consistent with the Polish artefacts are from samples of ores from the **multimetallic** deposits of the Erzgebirge. The group of metals plotted in the right corners of Figure 43 (1787/88, 1465/87, 302/83, 1304/87, 568/84, 16/82, 515/84, 3541/77, 1908/88 and 97/82) is consistent with mixed copper-lead-zinc deposits of Kirchberg near Pechtelsgrün in the central part of the Erzgebirge range. Another small group of objects (3543/77, 280/83, 1713/88, 1978/89, 1867/88, 1466/87, 1047/86, 1007/86, 1206/87, 1428/87, 1303/87, 1174 and 1185 (the last two are identical - perhaps they were made from the same piece of metal or ingot!) have lead isotope ratios consistent with their origin from the area of Freiberg (Grosschirma) in the N-E part of the Erzgebirge. Additionally 2 other objects might also belong two this group (1157/87 and a lead droplet 1371/87),

Table 16. Lead isotope composition and the assessment of origin of metal artefacts from Jakuszowice. The symbols describing alloy type are: AG - silver, Z - zinc, S - tin, P- lead, C - copper.

Object number	Pb 208/206	Pb 207/206	Pb 206/204	Origin	Alloy type
1143/66	2.08162	.84426	18.539	Freiberg/Joachimstahl	AG
1458/87	2.08549	.84518	18.544	Joachimstahl	AGCZ
1528/87	2.08963	.84752	18.499	Joachimstahl	AGCZP
3542/77	2.08683	.84588	18.525	Joachimstahl	AGCZP
3541/77	2.08960	.85008	18.431	Erzgebirge	CSP
3543/77/b	2.09169	.84931	18.444	Erzgebirge	CSP
1174/87	2.08648	.84417	18.542	Freiberg	CSP
1713/88	2.09156	.84564	18.532	Freiberg	CSP
1867/88	2.08954	.84624	18.514	Freiberg	CSP
280/83	2.09211	.84585	18.532	Freiberg	CSP
3543/77/a	2.09394	.84588	18.525	Freiberg	CSP
1787/88	2.09440	.84864	18.434	Saxony - Kirchberg	CSP
1303/87	2.08452	.84488	18.550	Schwarzwald-Schauinsland	CSP
304/83	2.17753	.92322	16.741	?Middle East?	CSZP
1908/88	2.08897	.85024	18.389	Erzgebirge	CSZP
568/84	2.08950	.84950	18.432	Erzgebirge	CSZP
97/82	2.08994	.85111	18.372	Erzgebirge	CSZP
1185/87	2.08648	.84417	18.542	Freiberg/Joachimstahl	CSZP
1007/86	2.08562	.84608	18.512	Joachimstahl	CSZP
1206/87	2.08716	.84648	18.522	Joachimstahl	CSZP
380/83	2.08763	.84684	18.495	Joachimstahl	CSZP
1822/88	2.09588	.85510	18.292	Sardinia - Sa Marchesa	CSZP
1304/87	2.09020	.84912	18.427	Saxony - Kirchberg	CSZP
1426/87 a	2.08206	.84334	18.548	Schwarzwald	CSZP
1426/87 b	2.08155	.84310	18.567	Schwarzwald	CSZP
303/83	2.08296	.84351	18.552	Schwarzwald	CSZP
469/84a	2.07888	.84140	18.629	Schwarzwald	CSZP
95/82	2.07625	.83896	18.678	Schwarzwald	CSZP
136/82	2.08512	.84312	18.591	Schwarzwald?	CSZP
369/83	2.10768	.86451	18.029	Sardinia - Perda s'Oliu	CZ
16/82	2.09506	.84959	18.455	Erzgebirge	CZP
1047/86	2.08954	.84522	18.545	Freiberg	CZP
1157/87	2.08844	.84407	18.597	Freiberg	CZP
1428/87	2.09022	.84647	18.524	Freiberg	CZP
1466/87	2.08974	.84520	18.539	Freiberg	CZP
1978/89	2.09151	.84602	18.528	Freiberg	CZP
1465/87	2.09227	.84882	18.438	Saxony - Kirchberg	CZP
302/83	2.09288	.84891	18.448	Saxony - Kirchberg	CZP
515/84	2.09304	.85082	18.396	Saxony - Kirchberg	CZP
110/82	2.07690	.83857	18.677	Schwarzwald	CZP

Table 16. continuation ...

Object number	Pb 208/206	Pb 207/206	Pb 206/204	Origin	Alloy type
1518/87	2.08277	.84122	18.640	Schwarzwald	CZP
2495/90	2.08441	.84192	18.649	Schwarzwald	CZP
320/83	2.07881	.83960	18.666	Schwarzwald	CZP
47/82	2.07963	.83968	18.660	Schwarzwald	CZP
989/86	2.07730	.83871	18.670	Schwarzwald	CZP
2/82	2.08588	.84323	18.579	Schwarzwald?	CZP
1371/87	2.09454	.84480	18.623	?	PB
1197/87	2.08507	.84775	18.424	Olkusz	PB
1275/87	2.08446	.84815	18.412	Olkusz	PB
1365/87	2.08825	.84798	18.466	Olkusz	PB
1778/87	2.08515	.84809	18.422	Olkusz	PB
216/82	2.08507	.84881	18.410	Olkusz	PB
227/82	2.08353	.84792	18.406	Olkusz	PB
1499/87	2.08717	.84805	18.447	Olkusz	PBAG
1390/87	2.08876	.84901	18.439	Olkusz	PBSN
1886/88	2.08633	.84754	18.419	Olkusz	PBSN
229/82	2.08460	.84786	18.420	Olkusz	PBSN
1212/87	2.08367	.84759	18.422	Olkusz	PBZN

but they rather stand out from the group of the other metals and might be of a different origin.

Three silver objects (1458/87, 1528/87 and 3542/77) are consistent with their origin from the famous silver deposits of Jachimov/Joachimstahl, whilst the silver fibula (1143/66) seems to be of a different origin.

The mineral deposits of Erzgebirge were well beyond the borders of the Roman Empire and there are no records known to me of their exploitation in Roman times. On the other hand "... until the first decades of the 20th century the Erzgebirge was in some way considered as a standard ore province throughout the world. Altenberg, Geyer, Ehrenfriedersdorf, Zinnwald-Cinovec, Krupka-Graupen and Krasno-Schlaggenwald served as examples for tin deposits..., but Freiberg, Annaberg, Schneeberg, Jachimov-Joachimsthal as classical veinbound polymetallic depositions." (Tischendorf 1989, 1). It has been mentioned before that these deposits were probably mined in the Bronze Age and during Celtic times. The Celtic copper-based metalwork was very sophisticated (Cunliffe 1976 and 1992) and in Western Europe the Romans followed their footsteps in mining. In his extensive assessment of the achievements of the Central European Celts, Jan Filip (1977) writes about the Boii Celts ('Bohemia' was derived from their name) that in the 2nd century BC they penetrated "...the South Bohemian barrow-grave region, where they sought new sources of raw materials, iron ore, alluvial gold ... and possibly also lead." Knowing the geology of this region one can be sure that the Boii found there also silver, copper, tin and calamine needed for making brass. The first documents describing the mining in the Erzgebirge date from 1168 AD (Baumann et al. 1986, 317) and since the Middle Ages until the beginning of this century the mining of tin, silver, copper, tin and zinc in the Erzgebirge was very extensive.

Three pieces of scrap bronze, a bronze fibula and a small bronze plate (136/82, 1426/87 a and b, 2/82 and 303/83) are consistent with the lead isotope

composition of a group of ores from the area of the Black Forest. The silver fibulae 1143/66 also seem to be consistent with this group of data. The area of the Black Forest is rich in lead-zinc-copper and silver minerals (Walther 1986, 188-191). It is known that in Roman times silver was extracted in Sulzburg and Badenweiler in the Southern Black Forest and lead would be plentiful as a by-product of silver extraction. Brass production in the Black Forest is also possible, because both copper and zinc minerals are found in the area.

8.6. Sources of non-ferrous metals in Western and Central Europe during the Late Roman period - conclusions based on the results of lead isotope analyses.

This chapter brought together lead isotope analyses of two groups of non-ferrous metals from Western and Central Europe excavated on sites of Roman period. The lead isotope 'fingerprints' of these metals were compared with the most important European metal deposits, and the best lead isotope match for the majority of artefacts was found amongst the multimetallic ores comparatively close to the sites. This result might seem obvious, but in fact it is for the first time possible with any degree of certainty to name specific mines as highly probable sources of metals in Roman Europe. The results obtained with lead isotope analysis also also in a new light the alloy production at that time, because they indicate that brass and leaded brass was very likely made from minerals present in one deposit. Further, the deposits used by the Gauls (Massif Central, Rheinische Schiefergebirge, Schwarzwald) were most likely chosen **because** of their mineralogical characteristics. The production of iron was also carried out in the same regions. There is very little evidence that the metal was imported to Gaul from other parts of the Roman Empire in large quantity, and lead from Britain, for example, was not used in making leaded alloys, but most probably just used as unalloyed metal (masonry clamps, anchors and lead pipes are very common), or possibly as lead-tin solder.

In fact it should not be too surprising that in the provincial part of the

Roman Empire the metals seem to originate from the closest mining region. After all "... Italy was able to export vast quantities of wine, oil and craft wares and was a rich **purchasing** centre for countless raw materials and luxury goods from all the various countries ..." (Heichelheim 1970, p.219). In this light the lead isotope analyses of metals from Rome itself should show the extremities of their varied origin; whilst the provincial metal supplies were most probably, well ... provincial.

The lead isotope analyses of metal artefacts from Poland presented here, are the first ever attempted on archaeological material from the area of Central Europe. So far there is no scientific evidence of the sources of non-ferrous metals used in this part of the world before the Middle Ages. The variety of origin of metals found in the Roman period strata in the settlement of Jakuszowice in Southern Poland confirms the excavator's evidence of numerous trade contacts of the people inhabiting this site, confirming that several metal objects are imported from the West and one probably from the East. The presence in Jakuszowice of metals which originate in Italy or Schwarzwald is not unexpected in view of the many other imported artefacts found on the site. The real surprise brought by the lead isotope data is the consistency of the origin of the **majority** of metal from the area of Saxony and Bohemia (Erzgebirge). From the geological and geographical point of view the Erzgebirge deposits are the closest, richest and mineralogically very suitable for the type of metal used in Roman times in Jakuszowice. Perhaps one can even say that this deposit, so famous and prolific in the Middle Ages, seems an obvious source of metal for this part of Europe. On the other hand, there seems to be no direct evidence for the exploitation of these deposits in the first centuries of our era. Bohemia was on the edge of the Celtic world and, in parallel with other Celt-dominated parts of Europe, iron smelting furnaces and slags were found there and provide the evidence of extensive local iron production. Jan Filip (1977, p. 113) concluded that the later La Tene

metal-founding techniques became the basis of Central European civilisation as such. Copper-based alloys were at that time much less important than iron in a practical sense; nevertheless, 'bronzes' are plentiful amongst all Celtic finds and sometimes bronze and iron are used side by side for the decorations on chariots and waggons. It would seem very strange if the Celts were not producing their own copper alloys and relied entirely on the Roman metal industry.

The archaeological evidence for the presence of Celts in Central Europe is mostly based on excavated burials and a few *oppida*, that is fortified Celtic settlements which were found in Bohemia. In the 1st century AD the Germanic tribes of Marcomanni over-ran the foothills of the Erzgebirge and their leader Marobud created a considerable military power on a Roman model (Filip 1977, p.196). Some archaeologists believe that the next two centuries brought the decline in population of this area and the disappearance of centralised political power which would support an organised metal production and distribution. However, Filip (1977, p.196) concluded that " ... It seems likely that the oppida in Bohemia continued their existence for some time under German overlordship at the beginning of the Christian era and that a number of Celtic workshops located in them continued production." In a similar way mining and metal extraction in the Erzgebirge might have carried on regardless of the overlords. The evidence provided by this preliminary lead isotope project needs much further research and perhaps it could lead to a considerable re-examination of the vision of Central Europe before the Christian era. Until now, the lack of written sources from the *Barbarian* side leaves the ancient historians only with a point of view projected by the Roman writers, most often from Rome. Roman disregard for people responsible for industry, and for foreigners in general, might have led to the omission of, or misinformation about many aspects of the metal production within and outside the Roman Empire.

No reliable information about the prehistoric exploitation of non-ferrous

ore deposits in Poland, former Czechoslovakia and East Germany has been published as yet. Until now, there has never been an archaeometallurgical project in this area which would provide material for the lead isotope studies in a way similar to the British Academy Project in the Mediterranean. For this reason the interpretation of the results of analyses of archaeological artefacts has to rely predominantly on the geological information and lead isotope data base. To establish an archaeologically satisfactory lead isotope data base of ores from the Bohemian Massif it is necessary to collect much larger number of samples from those parts of the deposit which might have been exploited in Roman times. The geological selection of samples for lead isotope analyses is guided by an interest in the type of the formation, dating and prospecting. For that purpose samples are often collected from unusual veins or outcrops, or from modern galleries cut at a depth of several hundred meters and then only single analyses from this selection, significant for the geology, are published. For archaeometallurgical research one would have to estimate which of the mines might have been worked in Roman (or earlier) times and find a good selection of ores relevant to this particular occurrence. Visits to the local mining museums might bring also much needed information and samples of ores.

Another interesting result of the lead isotope analyses is the uniform origin of lead samples from the workshop of Jakuszowice and their consistency with the lead ores of the Olkusz mining district of Polish Lower Silesia. South Poland is quite rich in metalliferous deposits (Osika 1986). The exploitation of flint in Prehistoric times and iron in the pre-Roman and Roman period has been well attested. However, nothing seems to be known about the exploitation of non-ferrous metals before the Middle Ages. Lower Silesia was mostly mentioned then for its gold and silver production. None of the silver pieces from Jakuszowice is consistent with their origin from the Olkusz galena. In fact no other metal, apart from lead, is consistent with the galenas from the Olkusz district. Why was only

lead smelted from these ores in the Roman period? The cupellation of silver has been known in Europe since the Bronze Age. On the other hand, the production of lead from galena is very simple and does not require much metallurgical knowledge; it is enough to roast pieces of galena in reducing conditions to obtain lead metal. Perhaps, in the 3rd century AD there were no metallurgists in Southern Poland who knew the craft of **smelting** non-ferrous metals and of cupellation? In Jakuszowice at least the non-ferrous metalwork seems to be limited to the art of producing metal objects from ready pieces of metal.

The metals from the site of Jakuszowice analysed for their lead isotope compositions include only a fraction of all metal found there. For example no Roman coins or fibulae of known Roman origin were analysed. The lead isotope compositions of these artefacts can bring further information about the Roman metal production and trade patterns and may show the present work in a different light. The artefacts left behind by ancient people represent a unique source of fully verifiable information about them and their times. This information should be extracted with the methods of the natural sciences and used in parallel with ancient written sources and other information obtained from archaeological excavations. It seems that lead isotope analyses can bring a new dimension to this research.

9. SUMMARY AND CONCLUSIONS.

The encyclopaedic description of archaeology lists as its aims: 1) the systematic description and study of antiquities and 2) the scientific study of the remains and monuments of the prehistoric period (Oxford Dictionary 1989). The second part of this description took a new meaning in the last thirty years when, in parallel with technical developments in the physical sciences, ancient artefacts became objects of much more sophisticated examination than ever before. Archaeometallurgy benefited in particular from the increased range and quality of various methods of elemental analyses. The first large analytical program was mounted in the late nineteen-sixties in Stuttgart - the aim of this study was to find the characteristics of metals from different periods and geographical areas through their chemical analysis in the hope of tracing their provenance. For nearly a decade this concept was tested by different scholars, until finally discredited by the overall failure to find any reliable elemental patterns in metals, which are relevant to their origin. Then, in the early eighties, lead isotopes entered the provenance scene. This method is firmly based in physics and geology, but its application to archeological materials is not as straight-forward as it might seem. This thesis has attempted to discuss the scientific foundations and methodology of this technique, bringing together all evidence available at present. In the second part there are given two, rather different, examples of its applications to archaeometallurgy.

Broadly speaking, the lead isotope compositions of metals can be used for provenance studies only if there is enough variation in the lead isotope characteristics of different ore deposits to allow their discrimination. In principle the variations amongst the lead isotope 'fingerprints' depend on the initial content of uranium and thorium in the ore forming fluids, and on the geological history of the deposit. The similarity, or otherwise, of the isotopic signatures of different ore deposits can be tested only by numerous mass spectrometric analyses of

the lead isotope compositions of the minerals. For the first time in this work it was possible to compare over 1,500 lead isotope data of ores from various European and Middle Eastern ore deposits directly related to archaeometallurgy. This comparison proved that the range of variations of their compositions is quite remarkable. However, to achieve their clear separation it is absolutely necessary to measure systematically **many** lead isotope ratios of minerals from each geological ore deposit. The geology and geochemistry must be at all times taken into account, and whenever possible, an archaeometallurgical study of the mining area should be conducted in parallel with the analytical work. The analyses of numerous samples from the same mineral deposit prove that (with rare exceptions) each occurrence has a strictly limited, and rather small, range of lead isotope compositions. With the help of statistical discriminant analysis of the three-dimensional lead isotope data, it is possible to distinguish the 'fingerprints' of nearly all ore deposits relevant to European archaeometallurgy which have so far been analysed. It is very important though, that samples used for the lead isotope characterisation of a mineral formation are accurately measured and that their choice is directly related to the parts and types of mineralisation which are relevant to the ancient metal-winning. These conclusions form the most important foundations of archaeological lead isotope provenance studies.

It is only about 15 years since uniform and reliable lead isotope data started to be published by geological laboratories. Recently, the accuracy of measurements increased considerably due to great improvements in the design of thermal ionisation mass spectrometers. The common use of international lead isotope standards allows cross-comparison of lead isotope measurements from different laboratories. From that standpoint recent lead isotope measurements of ore samples published in geological periodicals can be quite safely used for interpretation of archaeological provenance studies. However, the data published by geologists is hardly ever relevant to archaeological research; either the ore

deposits are irrelevant, or too few analyses are made for each deposit. In order to provide a firm data base for archeological projects it is necessary to establish an extensive and reliable lead isotope data base specifically for the needs of archaeology.

Lead isotope analyses of ancient slags from archaeological excavations and slag heaps are also essential. Their lead isotope characteristics cannot be treated in the same way as the 'fingerprints' of ore deposits from the statistical point of view, because the metal might have been smelted from ores of various origin. However, this information is essentially the direct link of metal with its production site and provides unique information about the organisation of metal production in antiquity. The Isotrace Laboratory at Oxford already has very good foundations for such a data base, but the work is far from finished, and requires more time, money and expertise.

Lead isotope analyses of ancient metal artefacts have been at present mostly confined to the Bronze Age metals. Finding the sources of ancient metals is not infallible; the lead isotope composition of a metal artefact, just like that of a mineral, represents in a sense a technological history of this metal. If the history is simple: lead comes to the metal from the ore and no other lead lead is added later, then the real source of this metal is reflected in its lead iostope composition. In the case of complicated technology - like for example, refining copper with lead or galena, a process which was commonly used in the last 500 years in Europe - the lead isotope composition will be that of the lead added to it. The interpretation of lead isotope data must always be looked at in the context of the time and place from which the artefact originates. There are three major problems facing lead isotope provenance studies of metals: the possibility of deliberate addition of lead to copper alloy (then only the origin of the lead, not copper, can be discovered); mixing of metals of different origin during the production of an object and mixing of different ores during metal smelting. Any

of these three activities would produce a misleading lead isotope 'fingerprint' of the metal. The first copper alloys were made with arsenic and later, tin. Lead was not deliberately added to the alloys until the first millenium BC, and the distances involved in the distribution of metals were fairly limited, therefore Bronze Age metal provenance studies using lead isotopes are the most advanced. Lead isotope research into the sources of metals and trade in the Bronze Age Mediterranean shows that only a few local ore deposits were exploited in a given area at any given time. There are always some artefacts which are made of imported metal, but so far there is no isotopic evidence of mixing of this metal with the local material. If the scrap, or broken objects, were melted together to produce new raw material, then either the melted metal was of one origin, or one of the types had a higher lead content which dominated the other one, because none of the groups of Bronze Age artefacts analysed so far shows a wide ranging and complex lead isotope pattern. Some other reasons behind this picture might include phasing out of the metals from circulation through burial customs, the repair (rather than melting) of existing artefacts, the use of small crucibles and 'hoarding' of imported objects. In any case, however, the possibilities of mixing of metals of different origin and alloying with lead must be always investigated during the interpretation of lead isotope data.

For this study I have examined the lead isotope characteristics of over 50 multimetallic ore deposits. The computerized data base allows quick and efficient visual and numerical comparisons of the data, and a close examination of these data shows that cases of two different deposits having nearly the same range of lead isotope ratios are very rare indeed. Many of the lead isotope 'fingerprints' of groups of ore samples fall close together and sometimes it might be difficult to decide visually which of them matches the composition of an ancient metal artefact. In such cases, however, if the number of analyses of ore samples is sufficient, then the numerical probability of the object's origin from

each of the groups of ores can be calculated using discriminant analysis. Such doubts as to the origin of the metal are usually related only to two or three deposits which have similar lead isotope characteristics, and then it is possible that in such cases the chemical (major and trace elemental) composition of the alloy can provide further evidence of the origin of the metal. Examination of a broad range of archaeological and geological evidence might also help in taking the final decision.

A quite new aspect of the earliest Mediterranean copper smelting emerged from the lead isotope analyses of early Minoan weapons and their comparison with the ores and ancient slags of the Eastern Mediterranean. The lead isotope 'fingerprints' of these metals suggest that they were made from several copper ore occurrences within the Aegean, but the metal might have been smelted only on two or three sites, where the ore was brought from the near-by small Cycladic occurrences. This conclusion is the first indication based on scientific evidence that, in spite of a comparative lack of mineral resources on Crete itself, the Minoans were able to have a local, reliable metal production. Some previous studies of the early Minoan daggers suggested the origin of their copper either in the Middle East or Cyprus. The power of lead isotope characterisation of copper based metals emerges fully from analyses of the Late Minoan weapons. These artefacts, which are a continuation and development of the Minoan tradition, show a dramatically different origin of metal. Suddenly, with the changes in local politics, and also the copper technology (tin bronze comes into use), the great majority of the weapons is fully consistent with their having been made with copper from Lavrion. The results presented here form only the tip of an iceberg in the research into changing trading networks in the Bronze Age Mediterranean, but even at this stage lead isotope 'fingerprinting' brings an important contribution to archaeological research.

The power of lead isotopes was even further tested on the example of

small scraps of metal, mostly dated to the Late Roman Period, excavated in Poland. The metals were found on a site where the presence of many imported objects proves extensive trading links with Roman Europe. The multimetallic copper based alloys were deliberately made at that time, and in most cases lead was a major addition. Since the Roman literary sources do not mention any metal production in Central Europe, it was expected that all of the metals found in Poland were imported from the Roman Empire. The metals were analysed for their alloy and lead isotope compositions. For comparison, lead isotope and chemical composition of a group of Gallo-Roman bronzes published by another laboratory was used. The alloy compositions of these two groups of metals are very similar, but their lead isotope ratios are quite different. Further comparisons of the lead isotope compositions of these metals with a wide range of ore deposits shows that the Gallo-Roman Bronzes are indeed consistent with their origin from the mines in the Massif Central and along the upper Rhine, but the Polish metals are distinctly different and their most probable source is in the mountains of the Erzgebirge in Central Europe. Also in this case the majority of metals in both, Gallo-Roman and Polish, groups does not show the wide scatter which would be characteristic of metal made from many different sources. Another interesting conclusion derived from the lead isotope and chemical analyses of these non-ferrous metals from Poland, is that the artisans making small objects seemed to be treating different types of copper alloys as if they were different materials; the alloy compositions are highly varied, which suggests that they were not melted together in one crucible and there is no evidence of addition of lead to copper alloys. In contrast to the copper and silver metals, which were brought from the regions of Bohemia and Saxony, lead metal from the site of Jakuszowice is consistent with its origin from the well known near-by lead-zinc-silver deposits near the town of Olkusz. This is the first indication of pre-Mediaeval exploitation of these ores.

The evidence gradually emerging from the lead isotope research extends the conclusions beyond a simple matter of where were the sources of metal used at a given time and how far did the metal travel; with carefully planned collaborative projects this scientific evidence can also provide an insight into the social organisation of prehistoric societies. There is no doubt that the power of lead isotope provenance studies increases dramatically with the number of analyses of archaeological and art-historical objects, and the coverage of mineral deposits relevant to the historical research. The data obtained for certain projects can provide very important information in a seemingly different field. One such example is the application of lead isotope measurements for authentification of objects of art. For example, it might be possible to combine the existing data base on the mineral deposits and metals with lead isotope analyses of lead-pigmented Roman glass and use it for comparison with collector's pieces to eliminate possible forgeries. A project on the sources of lead in the lead-white pigments used in different countries and periods is another possibility.

However, running a world-class isotope laboratory is very expensive and requiries a number of staff with an appropriate expertise. For this reason, the best use of the method and resources can be made only in a well funded laboratory, where a number of people work on several projects, because in this way the lead isotope data can be cross-compared and used for the interpretation of many different aspects of the material culture of the past.

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APPENDIX 1.
SHORT SPECIFICATION OF THE OXFORD MASS SPECTROMETER AND MEASURED VALUES OF THE NBS 981 LEAD ISOTOPE STANDARD.

APPENDIX 1.

SHORT DESCRIPTION OF THE ISOLAB 54 MASS SPECTROMETER IN THE ISOTRACE LABORATORY, UNIVERSITY OF OXFORD, AND MEASURED VALUES FOR THE NBS 981 LEAD ISOTOPE STANDARD.

1) General.

The spectrometer is a VG 38-54M Multicollector, forward Nier Johnson geometry [38cm electrostatic lens-54cm magnetic lens-30cm electrostatic lens: E-B-E] double-focusing mass spectrometer with an Isolab 54 Source, with a seven ion beam Faraday collector system on the focal plane after the magnetic lens and a Daly fast ion counting detector on axis after the 30cm electrostatic lens. The ultimate resolution with no loss of transmission is 3500. For operation with flat topped peaks the instrument can be operated at resolutions of 400, 600 and 1000. At a resolution of 400 (5% valley definition) the abundance sensitivity (mass 237 relative to mass 238) at the Daly detector is 0.15ppm, at an analyser pressure of $2x10^{-9}$ mbar. [The definitions of resolution and abundance sensitivity are given in Chapter 3]. The magnetic and electrostatic focusing fields are capable of a mass coverage, at 8kV source accelerating voltage, from 3 to 280 a.m.u.

The electronics and ion optics provided with the system are capable of focusing an ion beam generated in the thermal ionisation (TIMS), resonant ionisation (RIMS), secondary ionisation (SIMS) or glow discharge modes. The control electronics can be directly operated manually as well as through the computer keyboard. A manually operated System Analyser has been provided to monitor ion beams at the intermediate focal point of the mass spectrometer.

A motorised variable multiple collector has been supplied which accommodates a mass range of 11 per cent, sufficient to measure 40Ca, 42Ca, 43Ca and 44Ca simultaneously. The spectrometer has a 16 sample automatic turret, with VG separable type filaments and the possibility to use single, double and triple filament techniques, allowing 16 samples to be analysed in fully automatic TIMS mode. Two stabilised, computer controlled, filament current supplies each provide 0-8 amps with a stability of 15 ppm per hour and per degree centigrade.

Interchannel Faraday cup amplifier gain is reproducible to better than $\pm$10ppm per hour with respect to the axial channel. Intercup ion collecting efficiency biases are less than 50ppm. Interchannel amplifier calibration, using a high precision current source, is better than 10ppm.

The digitiser ADC system (used for digitising the ion currents for the seven Faraday cups) is linear to better than $\pm$2ppm and has a resolution of better than 1ppm when operated with a 5 sec. integration period.

The adjustable Multi-II collector head is provided with Peltier cooled amplifiers (with temperatures stabilised to $\pm$ 0.01^{o}C) and 7 collector channels (with positions along the focal plane adjusted and controlled under computer control) capable of measuring the isotope groups shown below:

LOW2	LOW1	AXIAL	HIGH1	HIGH2	HIGH3	HIGH4	
40		42		43		44	Ca
		63	65				Cu
84	85	86	87	88			Sr
	112	114	115	116	117	118	Sn
116	117	118	119	120	122	124	Sn
142	143	144	145	146	148	150	Nd
158	159	160	161	162	164	166	NdO
176	177	178	179	180			Hf
	184	185	187				Re
185	186	187	188	189	190	192	Os/Re
202	204	205	206	207	208		Pb
233	234	235	236	238	239		U
229	230	232					Th

The alignment of the ion optics together with the mid-analyser ion lenses, curvature and steering plates has been optimised so as to obtain maximum ion beam transmission with the mid-analyser ion lenses and steering plates set at very near zero volts, so that in ordinary TIMS operation at 500 resolution these plates can be connected to ground with no loss of transmission.

In the mass range 228 to 238 there is no change in baseline above 0.1ppm with or without ions in the spectrometer (other than genuine peaks or abundance sensitivity tailing). In addition there are no spurious baseline perturbations due to scattered or reflected ions or due to secondary electrons above 0.1ppm of the baseline, especially in the mass range 200 to 240. This feature is important for Uranium series disequilibrium dating.

The stability of the TIMS ion source EHT is better than 30ppm per hour. The control of the Magnetic Field is by means of a Hall effect probe and a 16 bit D.A.C. system, which achieves a magnetic field stability of better than 30ppm over 1 hour. The mass resettability is better than $\pm$60ppm in 1 second for a 6 mass unit jump at mass 88. The stability of voltages applied to the Electrostatic Analysers (for both the 38cm. and 30cm. ESA's) is better than 5ppm over 1 hour.

2) Vacuum System.

Source pumping is by a 1500 L/S (air) cryopump with metal sealed gate valve; a 24 hour Liquid nitrogen cold trap; a 2-stage rotary pump with catalytic foreline trap, liquid nitrogen trap, oil mist traps etc. The ultimate source pressure is better than 1 x 10-8 torr. The pumping speed of the source is to a pressure of less than 5 x 10-7 torr in 10 minutes from atmospheric pressure, and less than 5 x 10-8 torr in a further 20 minutes. The working pressure in the source is typically less than or equal to 5x10-8 torr when running Th samples on rhenium filaments at temperatures up to 1900 degrees C.

Analyser pumping is by 6 ion pumps totalling 600 L/S pumping speed, two titanium sublimation pumps and a liquid nitrogen cryoshield pump, to achieve a working vacuum (after bakeout) of 5 x 10-10 torr in the magnetic analyser.

3) Performance specifications.

a) The flatness of the peak top is better than ±1 part in 10,000 over ±240ppm in mass for all Faraday cups. For the Daly detector the peak is flat to better than ±1 part in 1000 over ±125ppm in mass.

b) The baseline noise is better than $2x10^{-16}$ Amps RMS for a 5 sec integration period for all Faraday collectors, using 10^{11} ohm measuring resistors. The amplifier gain stability is better than 20ppm over 30 minutes, whilst the amplifier time response after correction is to better than 10ppm of peak height in 2 seconds.

c) In the ion counting mode the Daly ion detection efficiency is greater than 95 per cent at a background rate of less than 0.1 counts per second; the linearity (with computer corrected dead time of about 13 nanoseconds) is better than ±0.25 per cent at count rates up to 3MHz.

d) The external reproducibility on the NBS987 Sr standard, 200ng load, is better than ±30ppm, 1 standard deviation [87/86 normalised to 88/86], on 8 samples, static and dynamic mode, using multicollection. Beam size is at least 3 x 10-11 Amps for the 88Sr beam, using the single Ta filament/phosphoric acid technique. The ratio 87/86 is in the range 0.71025 ± 0.00003, with application of an exponential fractionation correction.

As is recorded in TIMS Application Note TIMS 004, 10ng NBS987 strontium samples using a triple Ta-Re-Ta filament with phosphoric acid yield 88Sr beam intensities of 2 x 10-11 amps and a standard deviation of less than 30ppm on 8 samples.

As is recorded in TIMS Application Note 003, 1 microgram loads of NBS987 Sr run in multidynamic mode yield a standard deviation of about 10ppm for 8 samples.

e) When six samples each of the U010, U500 and U930 NBS uranium isotopic standards are measured, 2 microgram loadings, they show a system linearity better than 0.05 per cent, and external reproducibilities of less than 0.05 % [1 standard deviation].

f) The reproducibility of the 206/204 ratio (having a value of 2730) for the NBS SRM983 Pb standard is better than 0.3 per cent using the static mode, with 204Pb being measured by fast ion counting on the Daly detector.

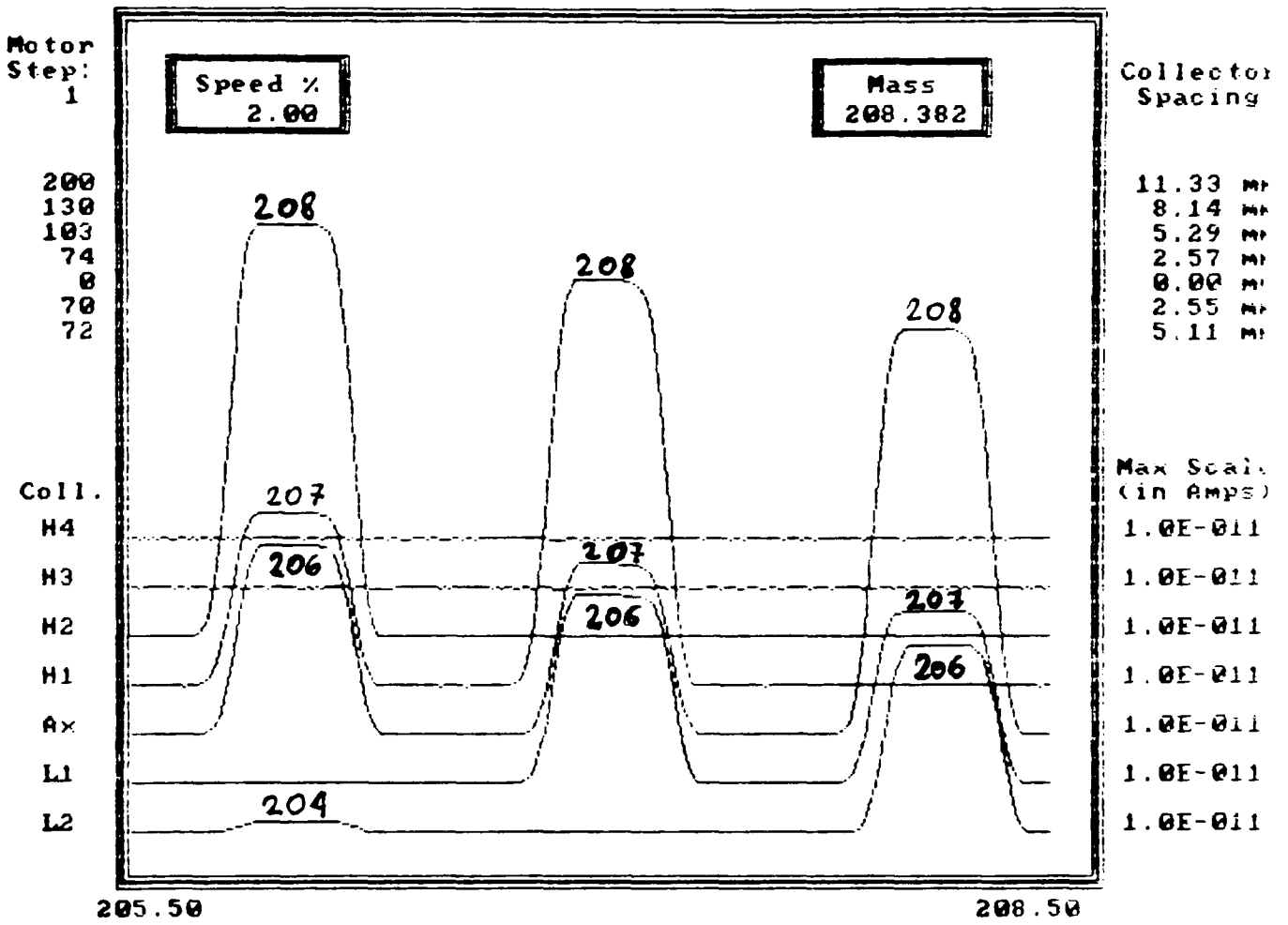
g) The reproducibility of 232Th/230Th ratios ranging from 1000:1 to 160,000:1, measured using the multicollector/Daly combination [ion counting] in static mode, is better than ±0.3 per cent.

h)Within statistical limits the 143Nd/144Nd ratio and the ratios 208Pb/204Pb, 207Pb/204Pb, 206Pb/204Pb do not depend on signal level.

i) The external reproducibility (bead to bead) for the NBS SRM981 Pb standard, 100ng samples, is better than ±0.05 per cent [1 standard deviation], using the static collection mode, on 8 samples, with an internal precision of less than ±0.02 per cent [1 standard deviation].

Typically the ion beam is about 4x10-12A on 206Pb for a 10ng sample of the NBS SRM981 Pb isotopic standard, and about 8x10-11A 208Pb for 200ng Pb when run at an appropriate

temperature, around 1200°C. Uniform mass fractionation figures (of about 1.0011) per atomic mass unit separation result from comparison of the three measured ratios with the standard ratios of [Todt]: 208Pb/204Pb = 36.7054; 207Pb/204Pb = 15.4925; 206Pb/204Pb = 16.9373; 207Pb/206Pb = 0.914699; 208Pb/206Pb = 2.16715.



Scan over the Faraday collectors for the four isotopes of Pb for the NBS isotopic standard SRM 981, showing the good separation between (and flat tops of) the ion beam peaks at a resolving power of 400.

LEAD STANDARD (NBS981) RUNS AT OXFORD (April-May 1992)

Note: Each set of ratios shows mean values calculated from 80 measurements run on different days, the samples were loaded according to Isotrace Laboratory standard procedure (out-gassed Re filament, Phosphoric acid and Silica Gel) by different people.

2.167150	0.914699	36.70540	15.49250	16.9373
2.158628	0.912539	36.49370	15.42731	16.90585
2.159865	0.912902	36.51538	15.43379	16.90628
2.160987	0.913070	36.55395	15.44499	16.91543
2.161705	0.913270	36.57272	15.45117	16.91878
2.162040	0.913409	36.58030	15.45426	16.91912
2.160916	0.913126	36.55784	15.44680	16.91773
2.160434	0.913100	36.53611	15.44139	16.91173
2.160200	0.913067	36.52889	15.43996	16.91027
2.160145	0.912980	36.53007	15.44226	16.91436
2.161595	0.913324	36.58370	15.45734	16.92402
2.161346	0.913275	36.56766	15.45242	16.91896
2.162842	0.913653	36.61244	15.46601	16.92786
2.160673	0.913158	36.54117	15.44409	16.9127
2.161927	0.913474	36.58933	15.46015	16.92454
2.159739	0.912919	36.50133	15.42891	16.90101
2.162984	0.913611	36.61553	15.46557	16.92787
2.159144	0.912787	36.49356	15.42769	16.90167
2.161961	0.913394	36.58374	15.45589	16.92137
2.161920	0.913396	36.57403	15.45229	16.91743
2.160687	0.913101	36.53723	15.44061	16.90962
2.159843	0.912957	36.51337	15.43420	16.90542
2.162253	0.913443	36.58772	15.45653	16.92121
2.162485	0.913523	36.59461	15.45884	16.92251
2.162809	0.913519	36.61615	15.46607	16.92963
2.162403	0.913401	36.60094	15.46019	16.92626
2.161955	0.913302	36.58679	15.45600	16.92332
2.160335	0.912822	36.56494	15.45015	16.92524
2.162982	0.913538	36.60520	15.46183	16.92337
2.160390	0.913086	36.54395	15.44532	16.91571
2.162149	0.913666	36.56458	15.45118	16.91144
2.163012	0.913861	36.59259	15.46028	16.91757
2.162142	0.913694	36.56488	15.45228	16.91181
2.163516	0.913960	36.60440	15.46330	16.9189
2.161887	0.913594	36.56358	15.45151	16.91307
2.163566	0.913885	36.61806	15.46755	16.92496
2.163337	0.913889	36.61374	15.46711	16.92446
2.162356	0.913672	36.57350	15.45362	16.91396
2.164020	0.914015	36.62752	15.47061	16.926
2.167150	0.914699	36.70540	15.49250	16.9373
2.158628	0.912539	36.49370	15.42731	16.90585
2.159865	0.912902	36.51538	15.43379	16.90628
2.160987	0.913070	36.55395	15.44499	16.91543
2.161705	0.913270	36.57272	15.45117	16.91878
2.162040	0.913409	36.58030	15.45426	16.91912
2.160916	0.913126	36.55784	15.44680	16.91773
2.160434	0.913100	36.53611	15.44139	16.91173
2.160200	0.913067	36.52889	15.43996	16.91027
2.160145	0.912980	36.53007	15.44226	16.91436
2.161595	0.913324	36.58370	15.45734	16.92402
2.161346	0.913275	36.56766	15.45242	16.91896
2.162842	0.913653	36.61244	15.46601	16.92786
2.160673	0.913158	36.54117	15.44409	16.9127
2.161927	0.913474	36.58933	15.46015	16.92454
2.159739	0.912919	36.50133	15.42891	16.90101
2.162984	0.913611	36.61553	15.46557	16.92787
2.159144	0.912787	36.49356	15.42769	16.90167
2.161961	0.913394	36.58374	15.45589	16.92137
2.161920	0.913396	36.57403	15.45229	16.91743
2.160687	0.913101	36.53723	15.44061	16.90962
2.159843	0.912957	36.51337	15.43420	16.90542
2.162253	0.913443	36.58772	15.45653	16.92121
2.162485	0.913523	36.59461	15.45884	16.92251
2.162809	0.913519	36.61615	15.46607	16.92963
2.162403	0.913401	36.60094	15.46019	16.92626
2.161955	0.913302	36.58679	15.45600	16.92332
2.160335	0.912822	36.56494	15.45015	16.92524
2.162982	0.913538	36.60520	15.46183	16.92337
2.160390	0.913086	36.54395	15.44532	16.91571

STATISTICAL EVALUATION OF THE NBS981 DATA.

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  ************
  * 8/6      *
  ************
```

			VALUE	ZSCORE	CASE #
		MAX	2.1671500	3.492	1
VARIABLE NUMBER	1	MIN	2.1586280	-1.875	2
NUMBER OF DISTINCT VALUES .	39				
NUMBER OF VALUES COUNTED. .	69		VALUE	VALUE/S.E.	
NUMBER OF VALUES NOT COUNTED	0	SKEWNESS	0.93	3.150	
		KURTOSIS	2.29	3.890	

```
                    EACH 'H' REPRESENTS     2 COUNTS
       H            EACH '-' REPRESENTS  5000E-7 UNITS
       HH
    H  HH           L =  2.15850
    HH HHH          U =  2.16750
   HHH HHH
   HHH HHH
 HHHHHHHHHHH     H
L-----------------U
```

	ESTIMATE	ST.ERROR		ESTIMATE
MEAN	2.1616050	0.0001911	ST.DEV.	0.0015877
MEDIAN	2.1618870	0.0002812	VARIANCE	0.0000025
MODE	NOT UNIQUE		RANGE	0.0085220
			(Q3-Q1)/2	0.0010271
TRIM(.15)	2.1615412			
HAMPEL	2.1615051		LOWER 95% C.L. OF MEAN	2.1612240
BWEIGHT	2.1614778		UPPER 95% C.L. OF MEAN	2.1619870
			Q1	2.1603900
TEST OF NORMALITY			Q3	2.1624440
W STATISTIC	0.9257		S-	2.1600170
SIGNIFICANCE LEVEL	0.0004		S+	2.1631930

```
          EACH '.' BELOW =       0.0001
              S  Q            Q    S
     M        -  1      HM M  3    +                        M
     I.................AE.E.................................A
     N                 MA D                                 X
                       PN I
-------------------------------------------------------------------------
```

STATISTICAL EVALUATION OF THE NBS981 DATA - continuation

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*************
* 7/6       *
*************
```

			VALUE	ZSCORE	CASE #
		MAX	0.9146990	3.399	1
VARIABLE NUMBER	2	MIN	0.9125390	-1.972	2
NUMBER OF DISTINCT VALUES .	39				
NUMBER OF VALUES COUNTED. .	69		VALUE	VALUE/S.E.	
NUMBER OF VALUES NOT COUNTED	0	SKEWNESS	0.94	3.178	
		KURTOSIS	2.02	3.419	

```
                    EACH 'H' REPRESENTS     2 COUNTS
     H              EACH '-' REPRESENTS  1500E-7 UNITS
     H H
     H HH           L =  .912300
    HHHHH           U =  .915000
    HHHHHH
   HHHHHHHH
  H HHHHHHHHH   H
L-----------------U
```

	ESTIMATE	ST.ERROR		ESTIMATE
MEAN	0.9133322	0.0000484	ST.DEV.	0.0004022
MEDIAN	0.9133240	0.0000702	VARIANCE	0.0000002
MODE	NOT UNIQUE		RANGE	0.0021600
			(Q3-Q1)/2	0.0002302
TRIM(.15)	0.9133051			
HAMPEL	0.9132970		LOWER 95% C.L. OF MEAN	0.9132355
BWEIGHT	0.9132932		UPPER 95% C.L. OF MEAN	0.9134288
			Q1	0.9130700
TEST OF NORMALITY			Q3	0.9135305
W STATISTIC	0.9378		S-	0.9129300
SIGNIFICANCE LEVEL	0.0029		S+	0.9137344

```
            EACH '.' BELOW =       0.0000
              S   Q               Q     S
 M            -   1      HM       3     +                              M
 I.........................AE.........................................A
 N                          MA                                        X
                            PN
--------------------------------------------------------------------------
```

STATISTICAL EVALUATION OF THE NBS981 DATA - continuation

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 ************
 * 6/4      *
 ************
```

			VALUE	ZSCORE	CASE #
		MAX	16.9373000	2.326	1
VARIABLE NUMBER	5	MIN	16.9010100	-2.026	16
NUMBER OF DISTINCT VALUES .	39				
NUMBER OF VALUES COUNTED. .	69		VALUE	VALUE/S.E.	
NUMBER OF VALUES NOT COUNTED	0	SKEWNESS	-0.13	-0.457	
		KURTOSIS	-0.45	-0.764	

```
                    EACH 'H' REPRESENTS     2 COUNTS
                    EACH '-' REPRESENTS  .002500 UNITS
          H
        H H         L =  16.8975
        H H         U =  16.9425
    H HHHH HHH
  H H HHHHHHHH
  H HHHHHHHHH  H
L-----------------U
```

	ESTIMATE	ST.ERROR		ESTIMATE
MEAN	16.9179000	0.0010037	ST.DEV.	0.0083377
MEDIAN	16.9187800	0.0015874	VARIANCE	0.0000695
MODE	NOT UNIQUE		RANGE	0.0362892
			(Q3-Q1)/2	0.0062351
TRIM(.15)	16.9183137			
HAMPEL	16.9182226		LOWER 95% C.L. OF MEAN	16.9159000
BWEIGHT	16.9180927		UPPER 95% C.L. OF MEAN	16.9199100
			Q1	16.9117700
TEST OF NORMALITY			Q3	16.9242400
W STATISTIC	0.9665		S-	16.9095700
SIGNIFICANCE LEVEL	0.1686		S+	16.9262400

```
            EACH '.' BELOW =      0.0005
                S   Q                       Q   S
 M              -   1          MHM          3   +                    M
 I.............................EAE.:.................................A
 N                             AMD                                   X
                               NPI
-------------------------------------------------------------------------

NUMBER OF INTEGER WORDS USED IN PRECEDING    PROBLEM    1450
```

APPENDIX 2.
UNPUBLISHED LEAD ISOTOPE DATA OF MEDITERRANEAN ORE DEPOSITS.

Z.A. STOS-GALE

APPLICATION OF LEAD ISOTOPE ANALYSIS TO PROVENANCE STUDIES IN ARCHAEOLOGY.

D.Phil. Thesis, 1992

Appendix 2 - Please note:

Lead isotope data for some of the ores listed in Appendix 2 have been superseded in the last four years by new, more accurate analyses. The definitive data on the ores from the Mediterranean is being gradually published since 1994 in *Archaeometry* and only data published in that journal should be used for any statistical or provenance research.

Zofia Stos-Gale

2 August 1996

Inv. Nos. etc	Region	Site	Main Constituent	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
KOL2 Chal	Chalkidiki	Kolombaki	Pb	2.06457	.83275	18.770
MADL1 Chal	Chalkidiki	Maden Lakkos	Pb	2.06755	.83316	18.809
TG38C Chal	Chalkidiki	Maden Lakkos	Pb	2.07067	.83423	18.768
MLH1 Chal	Chalkidiki	Maden Lakkos	Pb	2.06610	.83366	18.753
MLH2 Chal	Chalkidiki	Maden Lakkos	Pb	2.07135	.83383	18.799
MLH3 Chal	Chalkidiki	Maden Lakkos	Pb	2.06747	.83295	18.798
TG38a Chal	Chalkidiki	Maden Lakkos	Pb	2.06690	.83360	18.808
TG38c Chal	Chalkidiki	Maden Lakos	Pb	2.07067	.83423	18.768
MPH1 Chal	Chalkidiki	Mavros Petras	Pb	2.06687	.83383	18.754
MPH2 Chal	Chalkidiki	Mavros Petras	Pb	2.06952	.83431	18.787
OLY1 Chal	Chalkidiki	Olympias	Pb	2.06296	.83212	18.788
OLH1 Chal	Chalkidiki	Olympias	Pb	2.06618	.83449	18.757
TG40 Chal	Chalkidiki	Olympias	Pb	2.06920	.83483	18.762
STAG 2 Chal	Chalkidiki	Stagira	Pb	2.06739	.83377	18.786
STAG 3 Chal	Chalkidiki	Stagira	Pb	2.06820	.83367	18.784
PNG1	Crete	Panagia	Cu	2.08233	.84388	18.452
ANV	Crete, Central	Ano Varsamonero	Pb	2.09771	.85110	18.399
AN1	Crete, Central	Ano Varsamonero	Pb	2.09589	.85083	18.405
ANV100	Crete, Central	Ano Varsamonero	Pb	2.09519	.85033	18.394
VARS 1	Crete, Central	Ano Varsamonero	Pb	2.09393	.85058	18.436
C1	Crete, Central-South	Chrysostomos	Cu	2.08920	.85348	18.319
CHR1	Crete, Central-South	Chrysostomos	Cu	2.08969	.85084	18.393
CHR2	Crete, Central-South	Chrysostomos	Cu	2.07920	.84348	18.515
CHR3	Crete, Central-South	Chrysostomos	Cu	2.07834	.83913	18.573
CHR4	Crete, Central-South	Chrysostomos	Cu	2.07895	.84035	18.580
CHR4	Crete, Central-South	Chrysostomos	Cu	2.08103	.84077	18.599
CHR5	Crete, Central-South	Chrysostomos	Cu	2.08010	.84480	18.510
D (Lasaia 1)	Crete, Central-South	Lasaia	Cu	2.08554	.84286	18.544
LAS1	Crete, Central-South	Lasaia	Cu?	2.08554	.84286	18.544
LAF 1	Crete, Central-South	Lasaia	Pb	2.09281	.85031	18.381

Inv. Nos. etc	Region	Site	Main Constituent	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
LASF (Lasaia 1)	Crete, Central-South	Lasaia	Pb	2.07025	.84893	18.345
LEB1	Crete, Central-South	Lebena	Cu	2.08067	.84110	18.540
MES2	Crete, Central-South	Meskla	Cu	2.09862	.86201	18.054
MIAMOU A	Crete, Central-South	Miamou	Cu	2.07618	.84592	18.323
MIAMOU A2	Crete, Central-South	Miamou	Cu	2.09126	.85285	18.249
MIAMOU B	Crete, Central-South	Miamou	Cu	2.08389	.85033	18.233
LAQ	Crete, Central-South	Miamou	Pb	2.07676	.84019	18.591
MIAM 1	Crete, Central-South	Miamou	Pb	2.07745	.84033	18.614
MIAM 1	Crete, Central-South	Miamou	Pb	2.07765	.84058	18.583
MIC 1 (miamou c)	Crete, Central-South	Miamou	Pb	2.09048	.84236	18.698
CHR2	Crete, Eastern	Chrysokamino	Cu slag	2.05868	.83189	18.807
CHR3	Crete, Eastern	Chrysokamino	Cu slag	2.06808	.83722	18.640
SKL1	Crete, West-South	Sklavopoulou	Cu	2.08523	.84212	18.609
SKL2	Crete, West-South	Sklavopoulou	Cu	2.08624	.84495	18.485
SKL3	Crete, West-South	Sklavopoulou	Cu	2.08656	.84632	18.479
ANAPHI1 anap	Cyclades, Anaphi	Doumbaria Region	Pb	2.06382	.83077	18.888
ANA1 anap	Cyclades, Anaphi	Stavros region	Pb	2.06252	.83063	18.895
TG68 (1) antip	Cyclades, Antiparos	Not known	Pb	2.07656	.83481	18.807
TG68 (1) antip	Cyclades, Antiparos	Not known	Pb	2.07864	.83548	18.827
TG68 (1) antip	Cyclades, Antiparos	Not known	Pb	2.07956	.83549	18.832
TG68 (2) antip	Cyclades, Antiparos	Not known	Pb	2.08401	.83630	18.823
SA 23a antip	Cyclades, Antiparos	Not known	Pb	2.08047	.83374	18.966
SA 23b antip	Cyclades, Antiparos	A.Georghios	Pb	2.07784	.83812	18.734
AP1 antip	Cyclades, Antiparos	Agios Georgios	Pb	2.07618	.83510	18.805
AP2 antip	Cyclades, Antiparos	Agios Georgios	Pb	2.07710	.83538	18.804
AP3 antip	Cyclades, Antiparos	Agios Georgios	Pb	2.08011	.83574	18.819
AP4 antip	Cyclades, Antiparos	Agios Georgios	Pb	2.07686	.83514	18.804
AP6 antip	Cyclades, Antiparos	Agios Georgios	Pb	2.07656	.83481	18.807
AP7 antip	Cyclades, Antiparos	Agios Georgios	Pb	2.08401	.83630	18.823
AP8 antip	Cyclades, Antiparos	Agios Georgios	Pb	2.07956	.83549	18.832
AP9 antip	Cyclades, Antiparos	Agios Georgios	Pb	2.07864	.83548	18.827

Inv. Nos. etc	Region	Site	Main Constituent	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
SA23b antip	Cyclades, Antiparos	Agios Georgios	Pb	2.07784	.83812	18.734
2529 Anti	Cyclades, Antiparos	Almyra	Pb	2.07692	.83453	18.816
Orkos 1 kea	Cyclades, Kea	From J.Davis	Pb	2.07010	.83384	18.818
Orkos 2 kea	Cyclades, Kea	From J.Davis	Pb	2.06919	.83400	18.790
Orkos 3 kea	Cyclades, Kea	From J.Davis	Pb	2.06922	.83380	18.815
F 1W kea	Cyclades, Kea	Faros	Pb	2.07022	.83264	18.905
F 1X kea	Cyclades, Kea	Faros	Pb	2.06854	.83236	18.881
FAR 1 kea	Cyclades, Kea	Faros	Pb	2.06942	.83292	18.880
FAR 10 kea	Cyclades, Kea	Faros	Pb	2.06614	.83209	18.866
FAR 11 kea	Cyclades, Kea	Faros	Pb	2.06796	.83230	18.883
FAR 2 kea	Cyclades, Kea	Faros	Pb	2.06935	.83296	18.882
FAR 3 kea	Cyclades, Kea	Faros	Pb	2.06469	.83179	18.860
FAR 4 kea	Cyclades, Kea	Faros	Pb	2.06389	.83150	18.848
FAR 5 kea	Cyclades, Kea	Faros	Pb	2.06939	.83312	18.862
FAR 6 kea	Cyclades, Kea	Faros	Pb	2.06456	.83169	18.846
FAR 7 kea	Cyclades, Kea	Faros	Pb	2.06512	.83219	18.836
FAR 8 kea	Cyclades, Kea	Faros	Pb	2.06594	.83205	18.853
FAR 9 kea	Cyclades, Kea	Faros	Pb	2.06494	.83192	18.852
N 1W kea	Cyclades, Kea	Nikoleri	Pb	2.06919	.83243	18.893
N 1X kea	Cyclades, Kea	Nikoleri	Pb	2.07199	.83285	18.932
N 2W kea	Cyclades, Kea	Nikoleri	Pb	2.07087	.83266	18.920
NIK 1A kea	Cyclades, Kea	Nikoleri	Pb	2.06660	.83191	18.878
NIK 1B kea	Cyclades, Kea	Nikoleri	Pb	2.06452	.83164	18.858
NIK 1C kea	Cyclades, Kea	Nikoleri	Pb	2.07156	.83315	18.901
NIK 1D kea	Cyclades, Kea	Nikoleri	Pb	2.06644	.83216	18.880
NIK 1E kea	Cyclades, Kea	Nikoleri	Pb	2.06720	.83228	18.881
NIK 1F kea	Cyclades, Kea	Nikoleri	Pb	2.06587	.83226	18.852
NIK 2A kea	Cyclades, Kea	Nikoleri	Pb	2.06438	.83159	18.874
NIK 2B kea	Cyclades, Kea	Nikoleri	Pb	2.06723	.83252	18.866
NIK 2C kea	Cyclades, Kea	Nikoleri	Pb	2.07042	.83301	18.898
NIK 2D kea	Cyclades, Kea	Nikoleri	Pb	2.06569	.83223	18.851

Inv. Nos. etc	Region	Site	Main Constituent	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
NIK 2E kea	Cyclades, Kea	Nikoleri	Pb	2.06549	.83168	18.864
NIK 2F kea	Cyclades, Kea	Nikoleri	Pb	2.06316	.83136	18.846
NIK 2G kea	Cyclades, Kea	Nikoleri	Pb	2.06648	.83217	18.862
KGP1 kea	Cyclades, Kea	Petroussa	Pb	2.06338	.83165	18.839
KGP1 kea	Cyclades, Kea	Petroussa	Pb	2.06544	.83207	18.858
KJD1 kea	Cyclades, Kea	Petroussa	Pb	2.06153	.83122	18.854
KJD1 kea	Cyclades, Kea	Petroussa	Pb	2.06456	.83138	18.864
KJD1 kea	Cyclades, Kea	Petroussa	Pb	2.06662	.83180	18.883
PET5 kea	Cyclades, Kea	Petroussa	Pb	2.06338	.83182	18.861
PET6 kea	Cyclades, Kea	Petroussa	Pb	2.06461	.83170	18.864
PET7 kea	Cyclades, Kea	Petroussa	Pb	2.06390	.83158	18.861
PET8 kea	Cyclades, Kea	Petroussa	Pb	2.06531	.83181	18.861
PET9 kea	Cyclades, Kea	Petroussa	Pb	2.06565	.83183	18.869
PW kea	Cyclades, Kea	Petroussa	Pb	2.06757	.83194	18.890
PY kea	Cyclades, Kea	Petroussa	Pb	2.06784	.83201	18.892
TSL3 kyth	Cyclades, Kythnos	Lakkos	Cu, Fe	2.07207	.83551	18.735
TSL4 kyth	Cyclades, Kythnos	Lakkos	Cu, Fe	2.07458	.83532	18.759
TSL5 kyth	Cyclades, Kythnos	Lakkos	Cu, Fe	2.07016	.83712	18.678
TSL6 kyth	Cyclades, Kythnos	Lakkos	Cu, Fe	2.07111	.83432	18.791
MILYO 1 kyt	Cyclades, Kythnos	Milyes	Cu, Fe	2.06576	.83114	18.931
MILYO 2kyt	Cyclades, Kythnos	Milyes	Cu, Fe	2.06646	.83157	18.899
Zogo1 Kyth	Cyclades, Kythnos	Zoghaki	Cu	2.07162	.83468	18.820
Zogo2 kyth	Cyclades, Kythnos	Zoghaki	Cu	2.06972	.83397	18.819
Zogo3 kyth	Cyclades, Kythnos	Zoghaki	Cu	2.07016	.83426	18.813
491B nax	Cyclades, Naxos	from IGME	Pb	2.06539	.82983	18.932
491C nax	Cyclades, Naxos	from IGME	Pb	2.07041	.83024	18.982
AVY2	Cyclades, Seriphos	Avyssalos	Cu slag	2.08377	.83931	18.810
AVY3	Cyclades, Seriphos	Avyssalos	Cu slag	2.07606	.83803	18.736
AVY3	Cyclades, Seriphos	Avyssalos	Cu slag	2.07639	.83784	18.717
KEF 1	Cyclades, Seriphos	Kefala	Cu slag	2.06508	.83245	18.879
KEF 2	Cyclades, Seriphos	Kefala	Cu slag	2.07205	.83573	18.809

Inv. Nos. etc	Region	Site	Main Constituent	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
KEF 3	Cyclades, Seriphos	Kefala	Cu slag	2.06893	.83459	18.782
KONDO 1 ser	Cyclades, Seriphos	Kondouro	Cu	2.07016	.83408	18.810
SER1 (TG52A)	Cyclades, Seriphos	Moutoula	Pb	2.06344	.83094	18.942
SER2 (TG52A)	Cyclades, Seriphos	Moutoula	Pb	2.05998	.82975	18.871
SER3 (TG52B)	Cyclades, Seriphos	Moutoula	Pb	2.06255	.83057	18.893
SER4 (TG52B0	Cyclades, Seriphos	Moutoula	Pb	2.06121	.83032	18.899
TG 52 A1 ser	Cyclades, Seriphos	Moutoula	Pb	2.06521	.83081	18.908
TG 52 A3 ser	Cyclades, Seriphos	Moutoula	Pb	2.06349	.83044	18.897
TG 52 A4 ser	Cyclades, Seriphos	Moutoula	Pb	2.06202	.83029	18.892
TG 52 A5 ser	Cyclades, Seriphos	Moutoula	Pb	2.06238	.83026	18.885
TG 52 B1 ser	Cyclades, Seriphos	Moutoula	Pb	2.06280	.83030	18.890
TG 52 B2 ser	Cyclades, Seriphos	Moutoula	Pb	2.05909	.82965	18.856
TG 52 B3 ser	Cyclades, Seriphos	Moutoula	Pb	2.05937	.82970	18.861
NR7 (F7) siph	Cyclades, Siphnos	Ag. Ioannis	Pb	2.02427	.81862	19.167
TG43/10 siph	Cyclades, Siphnos	Ay. Sostis	Cu	2.08010	.83819	18.751
TG43/9 siph	Cyclades, Siphnos	Ay. Sostis	Pb	2.07945	.83831	18.714
TG43/IV/3 siph	Cyclades, Siphnos	Ay. Sostis	Pb	2.07844	.83814	18.743
TG71.1.1 siph	Cyclades, Siphnos	Faros	Pb	2.07797	.83803	18.687
TG71/2.2 siph	Cyclades, Siphnos	Faros	Pb	2.07981	.83839	18.739
TG43/12 siph	Cyclades, Siphnos	Mine 1	Pb	2.08138	.83903	18.731
TG53/1/a siph	Cyclades, Siphnos	Platia Gialos	Pb	2.07648	.83793	18.712
TG53/1/b siph	Cyclades, Siphnos	Platia Gialos	Pb	2.07511	.83774	18.690
SYR 17	Cyclades, Syros	Komito	Pb	2.07224	.83419	18.813
SYR 17A-1	Cyclades, Syros	Komito	Pb	2.07129	.83348	18.798
SYR 17A-2	Cyclades, Syros	Komito	Pb	2.07202	.83375	18.800
SYR 17A-3	Cyclades, Syros	Komito	Pb	2.07407	.83402	18.840
SYR 18	Cyclades, Syros	Komito	Pb	2.07533	.83437	18.853
SYR 18A-1	Cyclades, Syros	Komito	Pb	2.07195	.83394	18.800
SYR 18A-2	Cyclades, Syros	Komito	Pb	2.07509	.83391	18.854
SYR 2A	Cyclades, Syros	Rozos	Pb	2.06935	.83324	18.790
SYR 2B	Cyclades, Syros	Rozos	Pb	2.07438	.83453	18.818

Inv. Nos. etc	Region	Site	Main Constituent	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
SYR 2C	Cyclades, Syros	Rozos	Pb	2.07251	.83396	18.806
SYR 2D-1	Cyclades, Syros	Rozos	Pb	2.07186	.83395	18.803
SYR 2D-2	Cyclades, Syros	Rozos	Pb	2.07415	.83374	18.842
SYR 2D-3	Cyclades, Syros	Rozos	Pb	2.07425	.83470	18.805
SYR 3A-1	Cyclades, Syros	Rozos	Pb	2.07203	.83411	18.785
SYR 3A-2	Cyclades, Syros	Rozos	Pb	2.07153	.83409	18.780
SYR 3A-3	Cyclades, Syros	Rozos	Pb	2.07384	.83454	18.803
SYR 3A-4	Cyclades, Syros	Rozos	Pb	2.07487	.83462	18.807
SYR 3B	Cyclades, Syros	Rozos	Pb	2.07171	.83405	18.781
SYR 3C-1	Cyclades, Syros	Rozos	Pb	2.07341	.83458	18.798
SYR 3C-2	Cyclades, Syros	Rozos	Pb	2.07404	.83455	18.802
SYR 3C-3	Cyclades, Syros	Rozos	Pb	2.07208	.83420	18.788
SY1	Cyclades, Syros	Rozos, Ambellas, n.Grotto	Pb	2.07373	.83452	18.822
SY2	Cyclades, Syros	Rozos, Ambellas, n.Grotto	Pb	2.07558	.83493	18.852
SN 12 C ther	Cyclades, Thera	Athinios	Pb	2.06190	.82828	18.995
SN 17 A ther	Cyclades, Thera	Athinios	Pb	2.06179	.82821	18.997
SN 20 A ther	Cyclades, Thera	Athinios	Pb	2.05778	.82742	18.962
SN 20 B ther	Cyclades, Thera	Athinios	Pb	2.05892	.82757	18.974
SN 21 A ther	Cyclades, Thera	Athinios	Pb	2.05935	.82773	18.975
SN 21 C ther	Cyclades, Thera	Athinios	Pb	2.05871	.82754	18.970
SN 21 E ther	Cyclades, Thera	Athinios	Pb	2.05889	.82762	18.972
360B ther	Cyclades, Thera	Near cape Athinios	Pb	2.05387	.82638	18.981
GX ther	Cyclades, Thera	Near cape Athinios	Pb	2.05705	.82765	18.942
PH30o ther	Cyclades, Thera	Near cape Athinios	Pb	2.05571	.82660	18.950
PH91 ther	Cyclades, Thera	Near cape Athinios	Pb	2.05711	.82741	18.953
27708 tin	Cyclades, Tinos	Apigania	Pb	2.06823	.83626	18.732
27708 tin	Cyclades, Tinos	Apigania	Pb	2.07166	.83436	18.800
27711 tin	Cyclades, Tinos	from IGME	Pb	2.07185	.83426	18.799
27798 tin	Cyclades, Tinos	from IGME	Pb	2.07318	.83462	18.811
CH12 chio	East Sporades	Chios	Pb	2.10292	.85753	18.211
CH11 chio	East Sporades	Chios Agrelopos	Pb	2.10527	.85800	18.233

Inv. Nos. etc	Region	Site	Main Constituent	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
CHI3 chio	East Sporades	Rosoja Chios	Pb	2.10354	.85796	18.232
TG56 eub	Euboea	Almiropotamo, Vouno	Pb	2.06634	.83449	18.835
TG56 eub	Euboea	Almiropotamo, Vouno	Pb	2.06772	.83432	18.827
KALL 1 eub	Euboea	Kallianou	Pb	2.07893	.83957	18.666
TG59c eub	Euboea	Kallianou	Pb	2.08263	.84064	18.655
TG59e eub	Euboea	Kallianou	Pb	2.08054	.83971	18.667
TG59b eub	Euboea	Kallianou, Kordelia	Pb	2.07779	.83937	18.668
TG30 Maced dhaf	Macedonia	Dhafnoudhi	Pb	2.07383	.83638	18.818
TG37 Maced Met	Macedonia	Metallikon	Pb	2.10220	.85508	18.268
TG37 Maced Met	Macedonia	Metallikon	Pb	2.10220	.85508	18.269
PA2 Pangeon	Macedonia	Pangeon	Pb	2.07332	.83801	18.695
PA3 Pangeon	Macedonia	Pangeon	Pb	2.07543	.83844	18.695
TG34a Maced Pont	Macedonia	Pontokerasia	Pb	2.06994	.83277	18.854
TG4b Maced Pont	Macedonia	Pontokerassia	Pb	2.06991	.83257	18.818
G127a Psng Nik	Macedonia, Pangeon Mt.	Nikisiani Valley	Pb	2.07292	.83772	18.730
PANA Pangeon	Macedonia, Pangeon Mt.	Nikisiani Valley	Pb	2.06907	.83764	18.661
TG25 thas	N. Aegean, Thasos	Ay. Eleftherios	Pb	2.06854	.83416	18.751
V2 Thas	N. Aegean, Thasos	Kalirachi	Pb	2.07040	.83457	18.796
TG27 thas	N. Aegean, Thasos	Kalirachi, gallery		2.07131	.83423	18.764
KM1 thas	N. Aegean, Thasos	Koumaria	Pb	2.06906	.83461	18.764
KM3 thas	N. Aegean, Thasos	Koumaria	Pb	2.07088	.83468	18.774
KM2 thas	N. Aegean, Thasos	Koumaria, gallery	Pb	2.07118	.83502	18.781
K6thas	N. Aegean, Thasos	Kourlou	Pb	2.06896	.83405	18.779
A3 thas	N. Aegean, Thasos	Makrirarchi		2.07503	.83540	18.816
B3 thas	N. Aegean, Thasos	Makrirarchi		2.07018	.83460	18.788
C1 thas	N. Aegean, Thasos	Makrirarchi	Cu	2.07342	.83446	18.814
C2 thas	N. Aegean, Thasos	Makrirarchi	Cu	2.07075	.83473	18.800
MR2 thas	N. Aegean, Thasos	Marlou		2.06677	.83386	18.767
MR1 thas	N. Aegean, Thasos	Marlou	Pb	2.06726	.83406	18.780
IGME 49 thas	N. Aegean, Thasos	Sotiros	Pb	2.06842	.83409	18.782
TG28 thas	N. Aegean, Thasos	Sotiros	Pb	2.06974	.83391	18.778

Inv. Nos. etc	Region	Site	Main Constituent	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
VOUV Thas	N. Aegean, Thasos	Vouves		2.06927	.83393	18.780
VC Thas	N. Aegean, Thasos	Vouves	Cu	2.07551	.83578	18.819
TG24 thas	N. Aegean, Thasos	Vouves	Pb	2.06921	.83450	18.762
AG-1 Oth	Othrys Mountains	A. Georghios	Cu	2.10941	.86425	18.111
ANA Oth	Othrys Mountains	Anavra	Cu	2.09012	.85252	18.358
AA-2 Oth	Othrys Mountains	Ano Agoriani/A.Georghios	Cu	2.09332	.85480	18.271
KV-1 Othr	Othrys Mountains	Krio Vrisi, Kalamakia	Cu	2.08167	.84772	18.452
KV-2 Othr	Othrys Mountains	Krio Vrisi, Kalamakia	Cu	2.09312	.85329	18.355
KV-3 Othr	Othrys Mountains	Krio Vrisi, Kalamakia	Cu	2.09111	.85377	18.336
LIMO1 Othr	Othrys Mountains	Limogardion	Cu	2.08583	.85249	18.326
LIMO12 Othr	Othrys Mountains	Limogardion	Cu	2.08513	.85403	18.265
LIMO2 Othr	Othrys Mountains	Limogardion	Cu	2.08515	.85408	18.287
LIMO8 Othr	Othrys Mountains	Paleo Spartia	Cu	2.10732	.86932	18.039
PS Othr	Othrys Mountains	Paleo Spartia	Cu	2.10416	.85286	18.264
ST-3 Othr	Othrys Mountains	Stirfakas	Cu	2.09421	.85498	18.277
ST-7 Othr	Othrys Mountains	Stirfakas	Cu	2.08534	.84976	18.424
ANT3 Pel	Peloponnese	Ano Tiros	Pb	2.09461	.85247	18.377
AP-4 Pel	Peloponnese	Apidia	Cu	2.09441	.85081	18.468
ERAD 1	Peloponnese	Ermioni	Cu	2.08114	.85560	18.082
ERM 1	Peloponnese	Ermioni	Cu	2.08050	.85560	18.061
ERRO 1	Peloponnese	Ermioni	Cu	2.07935	.85387	18.113
ERTA 1	Peloponnese	Ermioni	Cu	2.06521	.84331	18.394
FL-2Pb Pel FL	Peloponnese	Floca	Cu, Pb	2.09259	.85160	18.443
K-2 Pel	Peloponnese	Krokees	Cu	2.09490	.85641	18.308
TY-1 Pel Ty	Peloponnese	Tyros village	Pb	2.09555	.85281	18.382
TY-3 Pel Kart	Peloponnese,Arcadia	Kartambabia, Tyros	Pb	2.09179	.85141	18.385
L-1 Pel	Peloponnese,Arcadia	Leonidion	Cu, Pb	2.04604	.82234	19.125
L-2 Pel	Peloponnese,Arcadia	Leonidion	Cu, Pb	2.05018	.82321	19.113
PQ-2 Arcadia	Peloponnese,Arcadia	Vlisithia	Cu, Pb	2.04633	.82225	19.123
4541 Mol	Peloponnese,Laconia	Molai	Pb	2.09441	.85277	18.400
4542 Mol	Peloponnese,Laconia	Molai	Pb	2.09261	.85181	18.384

Inv. Nos. etc	Region	Site	Main Constituent	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
4545 Mol	Peloponnese,Laconia	Molai	Pb	2.09245	.85191	18.390
4546 Mol	Peloponnese,Laconia	Molai	Pb	2.09311	.85233	18.396
4547 Mol	Peloponnese,Laconia	Molai	Pb	2.09362	.85205	18.389
4548 Mol	Peloponnese,Laconia	Molai	Pb	2.09380	.85248	18.374
4550 Mol	Peloponnese,Laconia	Molai	Pb	2.09568	.85307	18.413
EZM Mol	Peloponnese,Laconia	Molai	Pb	2.09269	.85199	18.390
M-2 Mol	Peloponnese,Laconia	Molai	Pb	2.09271	.85179	18.383
4544 Mol	Peloponnese,Laconia	Molai, Kotsaleika Zone	Pb	2.09549	.85259	18.391
TY-2 Pel Pap	Peloponnese,Laconia	Papadicenika	Pb	2.09447	.85179	18.407
PS11 (ARN) Rhod	Rhodope	Armoutsouk	Pb	2.07118	.83607	18.728
PS14 (MP.41) Bouk Rhod	Rhodope	Boukate	Pb	2.06963	.83615	18.731
PS15 (MP44)Bouk Rhod	Rhodope	Boukate	Pb	2.06581	.83568	18.708
GA 11 Ess	Rhodope	Essimi	Pb	2.07079	.83630	18.727
GA 204 Ess	Rhodope	Essimi	Pb	2.06778	.83547	18.719
GA 210 Ess	Rhodope	Essimi	Pb	2.07193	.83700	18.732
GA 242 Ess	Rhodope	Essimi	Pb	2.06947	.83573	18.725
GA 328A/195 Ess	Rhodope	Essimi	Pb	2.06919	.83588	18.734
GA 328A/244 Ess	Rhodope	Essimi	Pb	2.06889	.83583	18.730
GA 328A/247 Ess	Rhodope	Essimi	Pb	2.06850	.83582	18.733
GA 328A/57 Ess	Rhodope	Essimi	Pb	2.06934	.83587	18.724
GA 328A/91 Ess	Rhodope	Essimi	Pb	2.06857	.83573	18.734
GA 35 Ess	Rhodope	Essimi	Pb	2.06793	.83606	18.720
MY-1 Essim	Rhodope	Essimi	Pb	2.07081	.83619	18.752
MY-2 Essimi	Rhodope	Essimi	Pb	2.07205	.83673	18.639
PS10 (ATH) Kirki	Rhodope	from IGME	Pb	2.07211	.83690	18.752
PS6 (GAMMA) Kirki	Rhodope	from IGME	Pb	2.07381	.83693	18.691
GA04/233 Kir	Rhodope	Kirki	Pb	2.07444	.83695	18.688
GK 2/7 Kir	Rhodope	Kirki	Pb	2.07509	.83705	18.684
GK 6/6 Kir	Rhodope	Kirki	Pb	2.06943	.83683	18.687
GK 6/7 Kir	Rhodope	Kirki	Pb	2.07527	.83726	18.699
MA 44 Kirki	Rhodope	Kirki	Pb	2.06842	.83630	18.719

Inv. Nos. etc	Region	Site	Main Constituent	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
PS1 (SP 1) Kirki	Rhodope	Kirki	Pb	2.07519	.83750	18.695
PS12 (KA 1) Kir	Rhodope	Kirki	Pb	2.06894	.83559	18.728
PS12 (KA 1) Kir	Rhodope	Kirki	Pb	2.06905	.83547	18.730
PS13 Kir	Rhodope	Kirki	Pb	2.07003	.83560	18.729
PS2 (SP 2) Kirki	Rhodope	Kirki	Pb	2.07407	.83677	18.690
PS2 Kirki	Rhodope	Kirki	Pb	2.07508	.83689	18.701
PS3 Kirki	Rhodope	Kirki	Pb	2.07662	.83710	18.704
PS5 (GAMMA) Kirki	Rhodope	Kirki	Pb	2.07621	.83752	18.696
PS8 (GAMMA) Kirki	Rhodope	Kirki	Pb	2.07397	.83698	18.686
PS9 Kirki	Rhodope	Kirki	Pb	2.07464	.83692	18.686
PS16 (V129) Vir Rhod	Rhodope	Virini	Pb	2.06546	.83501	18.696
PS16 (V129) Vir Rhod	Rhodope	Virini	Pb	2.06756	.83554	18.713
TG49 sam	Samos	Ampelos (Nenedes)	Pb	2.05775	.82987	18.902
TG50A sam	Samos	Dhrakaioi, W. shore	Pb	2.06704	.83177	18.867
TG50B sam	Samos	Dhrakaioi, W. shore	Pb	2.06740	.83242	18.853
TG46 sam	Samos	from Gentner	Pb	2.12687	.87467	17.858
TG47 sam	Samos	from Gentner	Pb	2.12386	.87539	17.833
TG48 sam	Samos	Zestor, N. Shore	Pb	2.05958	.83084	18.872
PEB1 Volos BB	Thessaly	Bourboulithres, Pelion	Pb	2.06885	.83374	18.794
PEI1 delta Pelion	Thessaly	Pelion	Pb	2.06802	.83312	18.820
PEI1 Pelion	Thessaly	Pelion	Pb	2.06903	.83329	18.827
PEL3 Pelion	Thessaly	Pelion	Pb	2.06943	.83355	18.813
Trace Far	Thrace	Farasinon	Pb	2.07847	.83669	18.680
Trace Ias	Thrace	Iasmos	Pb	2.07536	.83663	18.716
Trace Kalo	Thrace	Kalotichon	Pb	2.08161	.83932	18.650
Trace Phil	Thrace	Philippi (Krenides)	Pb	2.07021	.83615	18.706

APPENDIX 3.
MULTIVARIATE DISCRIMINANT ANALYSIS OF CRETAN WEAPONS.

A. Division of the lead isotope data of the Early Minoan weapons into isotopically different groups. Probabilities of each artefact belonging to a given EMW group calculated by BMDP 7m.

	INCORRECT CLASSIFICATIONS	MAHALANOBIS D-SQUARE FROM AND POSTERIOR PROBABILITY FOR GROUP -				
GROUP EMW1		EMW1	EMW2	EMW3	EMW4	EMW5
CASE						
1		0.0 0.995	10.7 0.005	31.2 0.000	80.8 0.000	401.3 0.000
2		0.0 0.995	10.6 0.005	31.0 0.000	80.5 0.000	400.6 0.000
3		0.0 0.995	10.5 0.005	30.9 0.000	80.4 0.000	400.2 0.000
4		0.0 0.993	9.9 0.007	29.8 0.000	78.6 0.000	396.2 0.000
5		0.4 0.940	5.9 0.060	22.5 0.000	66.5 0.000	368.4 0.000
GROUP EMW2		EMW1	EMW2	EMW3	EMW4	EMW5
CASE						
6		4.7 0.121	0.8 0.872	10.2 0.008	43.7 0.000	311.6 0.000
7		5.2 0.089	0.6 0.901	9.6 0.010	42.3 0.000	307.7 0.000
8		9.9 0.007	0.0 0.918	5.0 0.076	31.8 0.000	278.4 0.000
9		11.2 0.003	0.1 0.881	4.1 0.116	29.6 0.000	271.7 0.000
10		13.7 0.001	0.4 0.769	2.8 0.230	25.9 0.000	260.1 0.000
11		14.1 0.001	0.5 0.746	2.6 0.253	25.3 0.000	258.3 0.000
GROUP EMW3		EMW1	EMW2	EMW3	EMW4	EMW5
CASE						
12	EMW2	17.1 0.000	1.1 0.549	1.5 0.451	21.6 0.000	246.2 0.000
13	EMW2	17.4 0.000	1.2 0.533	1.5 0.467	21.4 0.000	245.3 0.000
14		18.4 0.000	1.5 0.465	1.2 0.535	20.3 0.000	241.6 0.000
15		21.2 0.000	2.4 0.293	0.6 0.707	17.5 0.000	231.8 0.000
16		21.4 0.000	2.4 0.285	0.6 0.715	17.3 0.000	231.2 0.000
17		21.8 0.000	2.6 0.264	0.5 0.736	17.0 0.000	229.9 0.000
18		22.1 0.000	2.6 0.252	0.5 0.748	16.7 0.000	229.0 0.000
19		24.0 0.000	3.3 0.174	0.2 0.825	15.1 0.000	223.0 0.000
20		26.2 0.000	4.2 0.113	0.1 0.886	13.5 0.001	216.5 0.000
21		28.1 0.000	5.0 0.077	0.0 0.921	12.2 0.002	211.2 0.000
22		28.6 0.000	5.2 0.070	0.0 0.928	11.9 0.002	209.8 0.000
23		29.9 0.000	5.8 0.053	0.0 0.943	11.0 0.004	206.2 0.000
24		31.8 0.000	6.6 0.037	0.1 0.956	9.9 0.007	201.5 0.000
25		33.3 0.000	7.3 0.027	0.2 0.962	9.1 0.011	197.6 0.000
26		36.3 0.000	8.8 0.015	0.4 0.959	7.6 0.026	190.5 0.000
27		37.8 0.000	9.5 0.011	0.6 0.950	7.0 0.039	187.2 0.000
28		40.1 0.000	10.6 0.007	0.9 0.922	6.0 0.070	182.3 0.000
29		43.3 0.000	12.3 0.004	1.4 0.847	4.9 0.150	175.7 0.000
30		45.6 0.000	13.5 0.002	1.9 0.756	4.2 0.242	171.1 0.000
31		49.6 0.000	15.8 0.001	2.8 0.536	3.1 0.463	163.5 0.000
GROUP EMW4		EMW1	EMW2	EMW3	EMW4	EMW5
CASE						
32		56.1 0.000	19.5 0.000	4.4 0.201	1.7 0.799	152.3 0.000
33		61.4 0.000	22.7 0.000	6.0 0.072	0.9 0.928	143.9 0.000
34		63.3 0.000	23.9 0.000	6.6 0.049	0.7 0.951	141.0 0.000
35		63.4 0.000	23.9 0.000	6.7 0.048	0.7 0.952	140.8 0.000
36		69.2 0.000	27.6 0.000	8.6 0.015	0.2 0.985	132.5 0.000
37		70.1 0.000	28.1 0.000	9.0 0.012	0.2 0.988	131.3 0.000
38		79.6 0.000	34.2 0.000	12.5 0.002	0.0 0.998	119.0 0.000
39		88.6 0.000	40.2 0.000	16.3 0.000	0.4 1.000	108.5 0.000
40		104.8 0.000	51.3 0.000	23.6 0.000	2.1 1.000	92.1 0.000
41		129.6 0.000	69.1 0.000	36.1 0.000	6.7 1.000	71.3 0.000
GROUP EMW5		EMW1	EMW2	EMW3	EMW4	EMW5
CASE						
42		314.9 0.000	215.3 0.000	152.9 0.000	80.2 0.000	4.4 1.000
43		405.0 0.000	290.9 0.000	217.4 0.000	128.5 0.000	0.1 1.000
44		467.5 0.000	344.2 0.000	263.8 0.000	164.7 0.000	3.2 1.000

B. Probabilities (calculated by BMDP 7m) of each of the Early Minoan weapons originating from an ore deposit characterised by the most similar lead isotope 'fingerprint'. The museum numbers of objects can be identified from Table 8 by comparing with the BMDP numbers listed here.

	INCORRECT CLASSIFICATIONS	MAHALANOBIS D-SQUARE FROM AND POSTERIOR PROBABILITY FOR GROUP -			
GROUP EMW1		EMW1	LAVRIO	KYTLOW	
CASE					
111		1.6 0.809	8.6 0.024	4.8 0.166	
112	LAVRIO	0.7 0.496	0.7 0.504	18.4 0.000	
113	LAVRIO	2.9 0.191	0.0 0.809	26.5 0.000	
114		0.0 0.778	2.5 0.221	12.5 0.002	
115		1.9 0.760	9.2 0.019	4.3 0.221	
GROUP EMW2		EMW2	EMW3	KYTLOW	KYTHIGH
CASE					
47		2.8 0.607	13.3 0.003	3.6 0.390	18.6 0.000
48	KYTLOW	0.8 0.487	11.9 0.002	0.7 0.510	14.0 0.001
49		0.0 0.665	6.5 0.025	1.7 0.293	7.5 0.016
50		0.6 0.745	5.1 0.077	3.6 0.163	8.3 0.016
51		3.2 0.467	8.2 0.038	4.5 0.254	4.6 0.241
52		0.9 0.604	4.3 0.106	3.5 0.159	3.9 0.132
GROUP EMW3		EMW2	EMW3	KYTLOW	KYTHIGH
CASE					
53	EMW2	1.8 0.412	3.2 0.203	5.3 0.072	2.4 0.312
54	EMW2	1.5 0.431	1.9 0.359	6.1 0.045	3.4 0.166
55		2.0 0.353	1.5 0.457	7.0 0.028	3.6 0.162
56		2.9 0.186	1.0 0.483	8.3 0.013	1.8 0.319
57		3.0 0.176	1.1 0.449	8.2 0.013	1.6 0.362
58		3.2 0.158	1.1 0.451	8.5 0.011	1.4 0.380
59		3.3 0.150	0.8 0.521	8.9 0.009	1.7 0.321
60		4.4 0.087	0.3 0.689	11.1 0.003	2.6 0.221
61		5.6 0.047	0.1 0.739	13.0 0.001	2.6 0.212
62		6.2 0.030	0.0 0.660	13.7 0.001	1.6 0.310
63		8.3 0.020	0.8 0.888	17.1 0.000	5.3 0.092
64	KYTHIGH	8.5 0.012	2.8 0.197	14.6 0.001	0.1 0.790
65		8.2 0.011	0.2 0.612	16.3 0.000	1.2 0.376
66		14.1 0.004	3.2 0.965	24.9 0.000	10.0 0.031
67		16.3 0.002	3.9 0.970	27.9 0.000	10.9 0.029
68		24.5 0.001	10.0 0.994	37.7 0.000	20.5 0.005
69		14.6 0.001	1.6 0.862	25.5 0.000	5.2 0.137
70	KYTHIGH	15.3 0.001	2.6 0.384	25.1 0.000	1.7 0.615
71	KYTHIGH	17.6 0.000	4.5 0.214	27.2 0.000	1.9 0.786
72		19.9 0.000	3.4 0.728	32.0 0.000	5.4 0.271

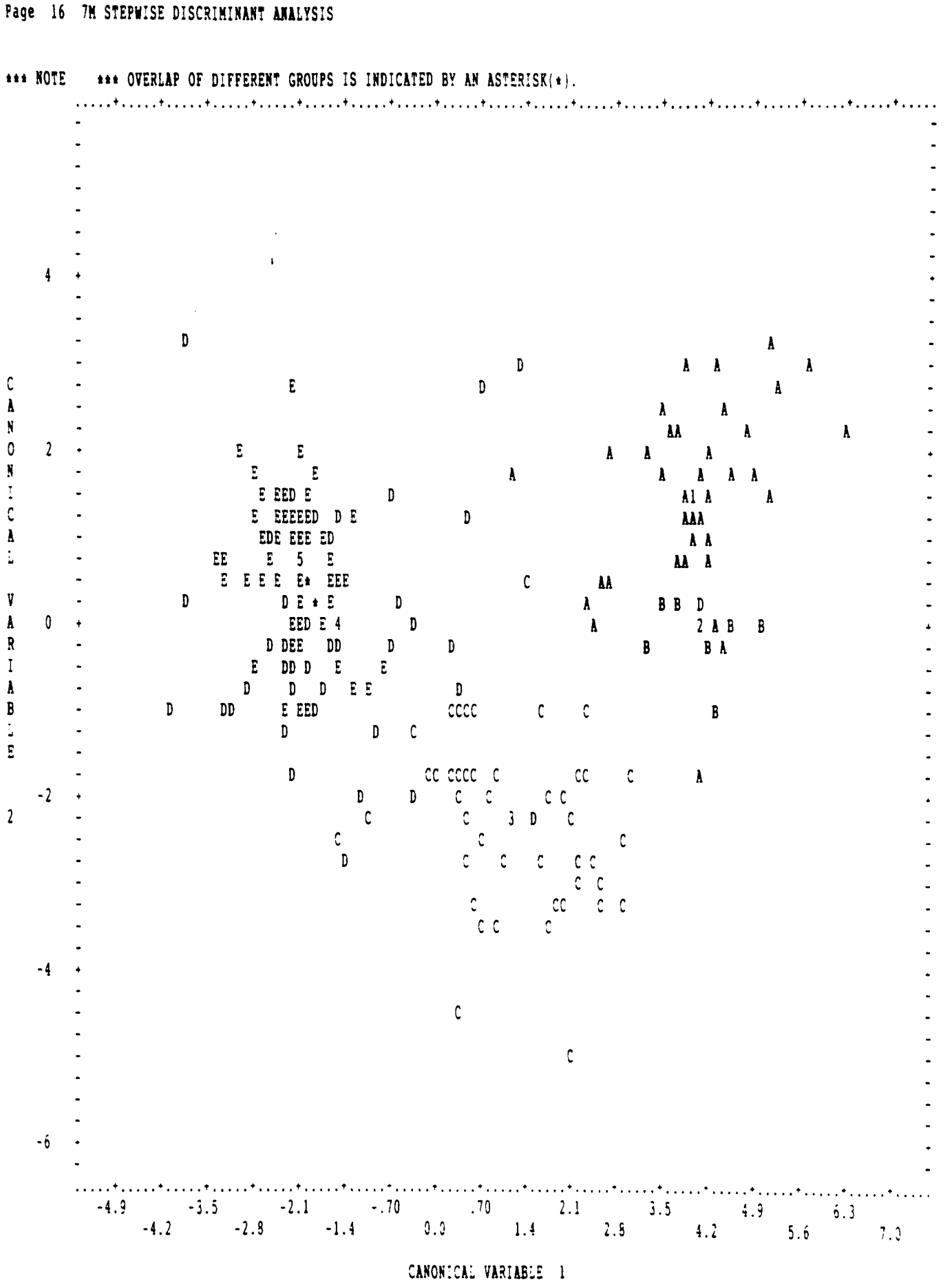
GROUP EMW4		CYPRUS	EMW4	CHRYSOST
CASE				
47		5.9 0.055	1.5 0.484	1.6 0.461
48		11.3 0.004	0.7 0.837	4.0 0.159
49	CHRYSOST	1.8 0.347	3.5 0.147	1.0 0.505
50		9.2 0.011	0.7 0.745	2.9 0.244
51	CHRYSOST	4.4 0.075	0.8 0.441	0.7 0.484
52	CHRYSOST	4.0 0.080	0.5 0.451	0.4 0.468
53		50.3 0.000	19.3 0.999	33.0 0.001
54	CHRYSOST	1.9 0.238	2.0 0.221	0.3 0.541
55		9.1 0.010	0.3 0.786	3.0 0.205
56		5.8 0.058	1.3 0.550	2.0 0.392

GROUP EMW5	EMW5	KURE	OTHRYS
CASE			
21	0.9 0.620	2.1 0.334	6.1 0.046
22	0.4 0.969	7.5 0.027	11.4 0.004
23	0.8 0.943	8.1 0.025	7.6 0.032

C. Probabilities of origin of the Late Minoan weapons from the deposits of Cyprus, Kythnos and Lavrion. The BMDP numbers are listed against the museum numbers in Table 10.

GROUP	crelmwe	CYPRUS	chrys	KYTHnos	crelmwe	lavrio
CASE						
1	KYTHnos	19.6 0.000	11.3 0.005	0.5 0.994	13.5 0.002	21.4 0.000
2		39.6 0.000	35.5 0.000	10.6 0.006	0.9 0.713	2.8 0.281
3	lavrio	38.2 0.000	42.5 0.000	26.7 0.000	3.7 0.214	1.1 0.786
4		48.3 0.000	41.9 0.000	11.9 0.010	3.1 0.760	5.5 0.230
5		45.8 0.000	36.6 0.000	7.2 0.461	7.0 0.498	12.0 0.041
6	KYTHnos	32.1 0.000	24.0 0.000	3.7 0.778	6.3 0.206	11.5 0.015
7	lavrio	65.5 0.000	76.1 0.000	57.8 0.000	18.7 0.028	11.6 0.972
8	lavrio	30.1 0.000	33.1 0.000	20.8 0.000	3.0 0.346	1.7 0.654
9	lavrio	30.8 0.000	33.4 0.000	19.0 0.000	1.5 0.379	0.5 0.621
10		43.1 0.000	41.0 0.000	15.7 0.000	0.8 0.544	1.2 0.456
11		17.3 0.001	14.9 0.003	5.9 0.237	3.9 0.636	7.2 0.124
12		32.2 0.000	26.6 0.000	5.9 0.138	2.6 0.731	6.0 0.131
13		40.2 0.000	32.7 0.000	6.5 0.274	4.7 0.653	9.1 0.073
14		56.4 0.000	52.7 0.000	20.4 0.000	3.6 0.512	3.7 0.487
15		39.8 0.000	37.0 0.000	13.7 0.001	1.3 0.607	2.2 0.392
16	lavrio	21.7 0.000	25.3 0.000	17.7 0.000	3.2 0.444	2.8 0.556
17		21.5 0.000	20.0 0.000	7.6 0.033	1.4 0.729	3.6 0.238
18		38.8 0.000	34.9 0.000	11.3 0.004	1.3 0.687	2.9 0.308
19	lavrio	72.0 0.000	68.5 0.000	30.2 0.000	9.1 0.410	8.4 0.590
20		43.9 0.000	40.6 0.000	14.1 0.001	1.4 0.636	2.5 0.362
21		25.1 0.000	23.3 0.000	8.3 0.016	0.7 0.713	2.7 0.271
22		48.4 0.000	43.4 0.000	14.6 0.002	3.0 0.667	4.4 0.331
23		39.5 0.000	35.7 0.000	10.9 0.005	0.9 0.708	2.7 0.287
24		42.3 0.000	40.2 0.000	15.3 0.000	0.7 0.550	1.1 0.449
25	lavrio	33.6 0.000	36.4 0.000	20.8 0.000	1.7 0.334	0.3 0.666
26		33.7 0.000	31.7 0.000	11.5 0.002	0.2 0.633	1.3 0.364
27	lavrio	46.9 0.000	44.6 0.000	19.1 0.000	3.0 0.482	2.8 0.518
28		36.3 0.000	36.7 0.000	17.0 0.000	1.8 0.513	1.9 0.487
29	lavrio	43.2 0.000	45.5 0.000	25.1 0.000	2.7 0.253	0.6 0.747
30	chrys	3.2 0.360	2.1 0.640	16.2 0.001	32.5 0.000	40.3 0.000
31		33.3 0.000	32.0 0.000	12.1 0.001	0.1 0.614	1.0 0.385
32		21.9 0.000	21.6 0.000	10.0 0.009	1.5 0.671	3.0 0.320
33	lavrio	59.4 0.000	55.4 0.000	22.8 0.000	5.2 0.472	5.0 0.528
34		36.9 0.000	36.3 0.000	15.3 0.000	0.3 0.509	0.3 0.490
35	CYPRUS	16.5 0.408	22.9 0.017	29.3 0.001	17.5 0.248	17.0 0.326
36	lavrio	41.4 0.000	40.9 0.000	18.3 0.000	1.0 0.433	0.5 0.567
37		53.0 0.000	49.4 0.000	19.0 0.000	3.0 0.523	3.1 0.476
38	lavrio	42.1 0.000	40.5 0.000	16.6 0.000	0.9 0.499	0.9 0.501
39		33.5 0.000	32.1 0.000	12.1 0.001	0.1 0.614	1.0 0.385
40	lavrio	38.8 0.000	39.1 0.000	20.7 0.000	3.8 0.404	3.1 0.596
41	lavrio	109.3 0.000	111.8 0.000	78.3 0.000	52.2 0.282	50.4 0.718
42	CYPRUS	9.9 0.935	18.2 0.015	28.2 0.000	17.3 0.024	17.1 0.026
43	KYTHnos	18.4 0.000	15.3 0.002	4.2 0.503	4.5 0.442	8.7 0.053
44		15.4 0.021	18.3 0.005	15.5 0.020	8.4 0.674	10.2 0.281

D. Plot of canonical variables of lead isotope ratios measured for the late Minoan Weapons and Aegean copper ores: A - Cyprus, B - Chrysostomos, C - Kythnos, D - Late Minoan weapons, E - Lavrio.



--- Plot 2 has been added to PLOTFILE.

APPENDIX 4.
LEAD ISOTOPE DATA USED FOR THE INTERPRETATION OF ORIGIN OF METALS FROM POLAND AND FRANCE.

Inv. No.	Region	Site	Description	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
BAYN 270 oxf	Bavaria	Bad Berneck	Galena	2.12114	.86253	18.159
BAYN 30 oxf	Bavaria	Bodenmais	Galena	2.13733	.88025	17.636
BAYN 30a oxf	Bavaria	Bodenmais	Galena?	2.14290	.88127	17.665
BAYN 360 oxf	Bavaria	Bodenmais	Galena	2.08543	.83580	18.670
BAYN 218a oxf	Bavaria	Erbendorf	Galena	2.09811	.85422	18.233
BAYN 182 oxf	Bavaria	Pfaffenreuth	Galena	2.13713	.88026	17.632
BAYN 182 oxf	Bavaria	Pfaffenreuth	Galena	2.13774	.88026	17.573
BAYN 188a oxf	Bavaria	Wittenau	Galena	2.08775	.84029	18.589
BAYN 249 oxf	Bavaria	Wollau	Galena?	2.08828	.85074	18.308
BAYN 285 oxf	Bavaria, Frankenwald	Wallenfels/Kronad	Galena	2.10289	.85870	18.154
GER 9b B	Bohemian Massif	Altenberg	Ga in granite	2.10934	.86119	18.118
CS 118 B	Bohemian Massif	Cernovice (Horsovsky Tyn)	Ga with qz	2.08357	.84678	18.451
CS 17 B	Bohemian Massif	Cinovec	Ga with qz, zinnw	2.10869	.86099	18.106
Biel 23 B	Bohemian Massif	Gersdorf, n. ROsswein	Ga with fluor.	2.08110	.84627	18.493
Biel 24 B	Bohemian Massif	Gersdorf, n. ROsswein	Ga with fluor.	2.07700	.84450	18.533
CS 122 B	Bohemian Massif	Jezdovice (Prague)	Ga with sph, qz, calc	2.10498	.86037	18.155
CS 126 B	Bohemian Massif	Jilove-Sohuliby (Prague)	Ga with chalc, qz.	2.10174	.86293	18.027
Biel 22 B	Bohemian Massif	Joachimstahl (Jahymov)	Ga with py	2.08614	.84579	18.481
CS 115 kh B	Bohemian Massif	Kutna Hora	Ga with sph, qz, calc	2.10472	.86065	18.134
CSSR 26 oxf	Bohemian Massif	Kutna Hora		2.09883	.85988	18.071
CS 124 B	Bohemian Massif	Marrachov	Ga with fl, ba	2.09269	.84775	18.417
CS 114 B	Bohemian Massif	Michalovice (Havlickuw Br	Ga with qz	2.09803	.85268	18.291
Biel 128 B	Bohemian Massif	Moldava, NW Teplice	Ga with chalc, qz	2.07590	.83890	18.638
CS 23L B	Bohemian Massif	Olovi	Ga	2.09088	.84909	18.418
CS 102 B	Bohemian Massif	Pribram	Ga with sp., carb, qz	2.10947	.86224	18.097
CS 71 B	Bohemian Massif	Pribram	Ga with reddish sp., carb, qz	2.10901	.86189	18.109
CS 106 B	Bohemian Massif	Pribram	Ga with py, qz, calc	2.10953	.86255	18.086
CS 10 B	Bohemian Massif	Pribram	Ga crystals	2.11059	.86369	18.055
CS 29/1 B	Bohemian Massif	Schlema n. Schneeberg	Gal with bar	2.08310	.84432	18.532
CS 29/2 B	Bohemian Massif	Schlema n. Schneeberg	Gal with bar	2.07923	.84371	18.529

Inv. No.	Region	Site	Description	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
CS 129 B	Bohemian Massif	Stribro	Ga with qz	2.08451	.84713	18.460
CS 21k B	Bohemian Massif	Stribro	Ga crystals	2.08665	.84887	18.395
CS 92 B	Bohemian Massif	Stribro	Ga with qz	2.08564	.84731	18.449
CS 96 B	Bohemian Massif	Stribro	Ga with qz, sph, ars	2.08594	.84758	18.445
CS 20k B	Bohemian Massif	Stribro	Ga	2.08750	.84783	18.446
CS 75 B	Bohemian Massif	Vrancice	Ga fi-gr, with sph, qz, calc	2.10890	.86150	18.116
CS 119 B	Bohemian Massif	Vyskov (Marianske Lazne)	Ga with qz	2.09474	.85359	18.314
GER 78 B	Bohemian Massif West	Krandorf nr. Nabburg Obpf	Ga with qz	2.09338	.85268	18.355
GER 76 B	Bohemian Massif West	Wolsendorf (Oberpfalz)	Ga with fl, ba	2.03501	.81970	19.140
GER 77 B	Bohemian Massif West	Wolsendorf (Oberpfalz)	Ga with fl	2.03323	.81925	19.142
Biel 65 B	Bohemian Massif, Saxony	Grosschirme n. Freiberg	Ga with py	2.09017	.84568	18.475
Biel 6/1 B	Bohemian Massif, Saxony	Kirchberg	Gal with chalc.	2.09349	.84929	18.420
Biel 6/2 B	Bohemian Massif, Saxony	Kirchberg	Gal with chalc.	2.09260	.85012	18.402
GER 13/1 B	Bohemian Massif, Saxony	Kirchberg	Ga coarse gr. with sid	2.11208	.86160	18.157
GER 13/2 B	Bohemian Massif, Saxony	Kirchberg	Ga coarse gr. with sid	2.11088	.86122	18.136
Biel 49 B	Bohemian Massif, Saxony	Zschopau	Ga	2.09570	.85051	18.376
Biel 51 B	Bohemian Massif, Saxony	Zschopau	pyrom	2.09841	.85144	18.356
GER 3b B	Erzgebirge	Ehrenfriedersdorf	Ga	2.04347	.81845	19.185
GER 1b B	Erzgebirge	Ehrenfriedersdorf	Ga with sph, chalc, sid, qz	2.11396	.86429	18.041
GER 4b B	Erzgebirge	Ehrenfriedersdorf	Ga	2.06283	.83220	18.796
BW 488a oxf	Erzgebirge	Freiberg	Galena	2.07132	.83918	18.607
BM B	Erzgebirge	Joachimsthal	Galena	2.08257	.84459	18.488
CSSR 25 oxf	Erzgebirge	Joachimsthal		1.90965	.78118	20.042
GER 3 B	Erzgebirge	Zinnwald	Ga coarse gr. with qz, zinnw	2.10906	.86159	18.091
GER 5b B	Erzgebirge	Zinnwald	Ga	2.10913	.86147	18.097
GER 14 B	Erzgebirge (east)	Hermsdorf	Ga fine gr, foliated	2.14348	.88494	17.556
GER 324a B	Erzgebirge (east)	Hermsdorf	Ga fine gr	2.14158	.88528	17.538
Hals62 B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	Ga fine gr.,with chalc., qz.	2.09818	.85222	18.304
Hals55 B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	Ga with chalc., qz.	2.10160	.85372	18.287
Hals59 B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	Ga fine gr.,with chalc., qz.	2.10155	.85336	18.297
Hals57 B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	Ga with chalc., qz.	2.10071	.85326	18.291

Inv. No.	Region	Site	Description	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
Hals35 B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	ga. qz.	2.09485	.84897	18.387
Hals56 B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	Ga crystals	2.09369	.84773	18.434
Hals28 B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	Ga in crystals of fl.	2.09952	.84991	18.409
Hals2A B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	coarse-gr.Ga with fuorite	2.09156	.84943	18.370
Hals3A B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	Ga with Ca-baryte	2.09955	.85305	18.292
Hals4A B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	coarse gr Ga with fl.	2.10143	.85291	18.308
Hals54 B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	coarse-gr Ga in qz	2.10206	.85253	18.343
Hals53 B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	Ga in qz	2.10132	.85245	18.319
Hals58 B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	Ga with fl.	2.09911	.85134	18.344
Hals61 B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	Ga with fl.	2.09645	.85023	18.362
Hals60 B	Erzgebirge, Freiberg	Halsbrucke, Beihilfe mine	Ga with fl.	2.09735	.85114	18.326
HARZ 89 oxf	Harz		Galena	2.09661 •	.85711	18.215
Biel 98 B	Harz	Bad Grund	Ga with sph, qz	2.08452	.84720	18.469
Biel 97 B	Harz	Bad Grund	Ga with qz, tetra	2.08563	.84750	18.452
HA58 oxf	Harz	Bad Grund, Wiedemannsbuch	Pb/Zn ore with Ag	2.08106	.84721	18.429
Biel 9k B	Harz	Bad Grund/Iberg	Ga	2.08599	.84740	18.467
Biel 138 B	Harz	Beerberg-Hasserode	Ga, sph, py, chalc, calc	2.08443	.84838	18.454
Biel 10k B	Harz	Clausthal	Ga	2.08259	.84585	18.502
Biel 11 B	Harz	Clausthal	Ga in qz	2.08224	.84578	18.506
Biel 5k B	Harz	Clausthal	Ga coarse gr	2.08628	.84754	18.464
Biel 140 B	Harz	Gernrode	Ga, sph, py, chalc	2.08924	.84954	18.490
Biel 31 B	Harz	Harzgerode	Federerz with Qz, Py	2.08431	.84970	18.397
Biel 36 B	Harz	Harzgerode	Bour crystal	2.08193	.84862	18.431
Biel 141 B	Harz	Hayn	Ga with sid, sph	2.08237	.84635	18.498
Biel 14k B	Harz	Hohwerte-Gernrode	Ga with fl	2.07400	.83970	18.630
Biel 15k B	Harz	Hohwerte-Gernrode	Ga with fl	2.07730	.84140	18.563
ND 183 oxf	Harz	Lautenthal	Galena	2.07848	.84475	18.463
Biel 7k B	Harz	Lauterthal	Ga	2.08269	.84520	18.527
Biel 91 B	Harz	Lauterthal	Ga with sph, chalc, qz, calc	2.08100	.84470	18.519
Biel 33 B	Harz	Lerbach, Western Harz	Cl with carb	2.07830	.84573	18.545
Biel 11k B	Harz	Neudorf	Galena crystals	2.08532	.84860	18.389

Inv. No.	Region	Site	Description	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
Biel 12k B	Harz	Neudorf	Galena cleavage pieces	2.08460	.84934	18.413
Biel 17a B	Harz	Neudorf	Galena with sider	2.08456	.84935	18.413
Biel 26 B	Harz	Neudorf	Galena with sider, qz.	2.08499	.84916	18.437
Biel 6a B	Harz	Neudorf	Galena with sid.	2.08532	.84860	18.389
ND 121 oxf	Harz	Oberschulenberg	Galena	2.08169	.84631	18.423
Biel 10a B	Harz	Pfaffenberg	Galena with chalc., qz, sph.	2.08314	.84881	18.414
Biel 74 B	Harz	Pfaffenberg	Gal. with carb, qz., sph.	2.08425	.84947	18.421
Biel 8k B	Harz	Radautal	Ga with silicates	2.08439	.84785	18.462
ND 177 oxf	Harz	Rammelsberg		2.09006	.85551	18.215
ND 182 oxf	Harz	Rammelsberg	Galena in schist	2.08890	.85539	18.218
ND 189 oxf	Harz	Rammelsberg		2.08959	.85543	18.219
ND 192 oxf	Harz	Rammelsberg		2.08849	.85518	18.201
ND 185 oxf	Harz	Rammelsberg	Pyrite?	2.08923	.85528	18.216
ND 194 oxf	Harz	Rammelsberg		2.08937	.85515	18.224
ND 179 oxf	Harz	Rammelsberg		2.08891	.85528	18.215
HA6le/1 oxf	Harz	Rammelsberg/Goslar	Galena	2.08927	.85546	18.213
HA6le/1 oxf	Harz	Rammelsberg/Goslar	Galena	2.08933	.85586	18.220
Biel 2 B	Harz	Rammelsberg	Galena massive, redepositioned	2.09403	.85665	18.243
Biel 2k B	Harz	Rammelsberg	Galena in brown ores	2.09319	.85616	18.243
Biel 3k B	Harz	Rammelsberg	Galena in crystals	2.09019	.85520	18.294
Biel 1K B	Harz	Rammelsberg	Galena	2.09246	.85612	18.245
Biel 104 B	Harz	St. Andreasberg	Ga with carb.	2.08276	.84544	18.511
Biel 4k B	Harz	St. Andreasberg	Ga coarse gr.	2.08406	.84637	18.499
Biel 6k B	Harz	St. Andreasberg	Ga	2.08196	.84509	18.533
JD04 har oxf	Harz	St. Andreasberg	Galena	2.08274	.84880	18.418
ND 103 oxf	Harz	St. Andreasberg		2.07981	.84543	18.433
Biel 80 B	Harz	St. Andreasberg	Ga with sph., calc	2.08156	.84509	18.527
Biel 139 B	Harz	Stolberg	Ga, sph, sid	2.08458	.84857	18.444
Biel 25 B	Harz	Strassberg-Siptenfelde	Ga with qz., carb.	2.08393	.84822	18.467
Biel 142 B	Harz	Suplingen	Ga, py, chalc, bar	2.09596	.85259	18.425
Biel 143 B	Harz	Suplingen	Ga, bar, fl, qz	2.08850	.85138	18.362

Inv. No.	Region	Site	Description	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
Biel 89 B	Harz	Thumkuhlrnthal	Ga with lim	2.08183	.84833	18.441
Biel 5a B	Harz	Tilkerode, Eastern Harz	Cl with carb	2.07550	.84505	18.545
Biel 137 B	Harz	Trautenstein	Ga, chalc, calc,qz	2.08493	.84941	18.427
Biel 34 B	Harz	Wolfsberg	Federerz	2.08300	.84854	18.421
Biel 37 B	Harz	Wolfsberg	Bour with qz.	2.08300	.84854	18.490
Biel 43 B	Harz	Wolfsberg		2.08249	.84816	18.477
Biel 39 B	Harz	Wolfsberg	tin???	2.08215	.84575	18.427
143b hess B	Hess			2.08112	.84485	18.481
H10 oxf	Hess	Bad Ems, Friedrichssegen	Pb, Zn with Ag	2.08192	.85504	18.368
H10 he oxf	Hess	Bad Ems, Friedrichssegen	Pb, Zn with Ag	2.08451	.85085	18.304
H9he oxf	Hess	Bad Ems, Friedrichssegen		2.08835	.85491	18.235
HESS 116a oxf	Hess	Bad Ems/Pfingstwiese	Galena	2.09188	.85678	18.178
HESS 116e/1 oxf	Hess	Bad Ems/Pfingstwiese	Galena	2.09141	.85257	18.332
Biel 144 B	Hess	Bensberg, Bergisches Land	Massive ga	2.09604	.85872	18.170
Biel 150 B	Hess	Bleialf, n. Trier	Ga massive	2.08479	.84978	18.386
Biel 153 B	Hess	Bleialf, n. Trier	Ga massive	2.08535	.85007	18.395
H109c oxf	Hess	Braubach, Rosenberg	Galena	2.09055	.85695	18.227
H109f oxf	Hess	Braubach, Rosenberg	Galena	2.09067	.85672	18.204
H109j oxf	Hess	Braubach, Rosenberg	Galena	2.08950	.85614	18.218
Biel 146 B	Hess	Ems	Massive ga	2.08919	.85572	18.242
H113a oxf	Hess	Heftrich, Hannibal Mine	Galena	2.08054	.84511	18.457
H2 oxf	Hess	Heftrich, Hannibal Mine	Galena?	2.08055	.84496	18.470
H28 oxf	Hess	Heftrich, Roman Fort	Galena	2.08237	.84570	18.437
H110c oxf	Hess	Holzappel		2.08583	.85471	18.227
Biel 90 B	Hess	Holzappel, near Nassau	Ga, sph, chalc, tetra	2.09071	.85577	18.256
H100 oxf	Hess	Kaisergrube	Galena?	2.07979	.84582	18.447
H101 oxf	Hess	Kaisergrube,	Galena	2.08191	.84525	18.478
Biel 149 B	Hess	Littfeld, Musen area	Massive ga with calc	2.09935	.85931	18.189
Biel 159 B	Hess	Marialinden, n. Bensberg	Foliated ga	2.09995	.85944	18.220
Biel 156 B	Hess	Mittelagger, Bensberg	Ga	2.08761	.84833	18.454
Biel 151 B	Hess	Nassau	Ga with qz	2.09815	.85819	18.257

Inv. No.	Region	Site	Description	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
H21a oxf	Hess	Nida Fort		2.08446	.84982	18.352
H65a oxf	Hess	Nida Fort		2.08423	.84961	18.365
Biel 152 B	Hess	Niederfischbach,Betzdorf	ga with sid, chalc.	2.09709	.85858	18.220
Biel 158 B	Hess	Ramsbeck	Ga massive foliated	2.09368	.85642	18.254
Biel 105 B	Hess	Siegerland	Ga with qz	2.08605	.84833	18.454
HESS 96a oxf	Hess	Sommerkahl Mine, Hosbach	Galena, Pyrite?	2.06086	.83109	18.781
HESS 94 R2 oxf	Hess	Usingen, Philippseck		2.07960	.84360	18.497
Biel 17k B	Hess	Wetzlar	Massive ga	2.09759	.85829	18.249
BW 2 oxf	Hess, Heidelberg	Wiesloch		2.06565	.83457	18.775
BW 2 wie oxf	Hess, Heidelberg	Wiesloch	Galena	2.07159	.83648	18.691
BW 40e oxf	Hess, Heidelberg	Wiesloch		2.06985	.83615	18.718
BW 425 oxf	Hess, Heidelberg	Wiesloch	Galena	2.07156	.83617	18.706
BW 428a oxf	Hess, Heidelberg	Wiesloch		2.07108	.83625	18.719
ND 38 oxf	Hesse/Rhineland	Bergisches Land,Luderich		2.08980	.85408	18.241
ND 27 oxf	Hesse/Rhineland	Bergisches, Untereschbach	Galena	2.09601	.85908	18.113
F33ber	Massif Central, South	Montagne Noire	Galena, sphaler, sider	2.12152	.87179	17.940
F28bib	Massif Central, South	Montagne Noire	galena, small mine	2.12277	.87277	17.920
F15br	Massif Central, South	Montagne Noire	Sph, gal many other sulph	2.12725	.87782	17.760
F13cam	Massif Central, South	Montagne Noire	Galena, qz small prospect	2.08293	.84824	18.450
F32cam	Massif Central, South	Montagne Noire	Gal/diss. sph, small working	2.12570	.87542	17.820
F30con	Massif Central, South	Montagne Noire	Gal/diss. sph, small dep.	2.12310	.87634	17.790
F14cus1	Massif Central, South	Montagne Noire	Galena/barite vein	2.12809	.87809	17.800
F14cus2	Massif Central, South	Montagne Noire	Galena/barite vein	2.12802	.87760	17.810
F29flm	Massif Central, South	Montagne Noire	Gal/diss. sph, small prospect	2.12067	.87263	17.900
F24lou	Massif Central, South	Montagne Noire	Galena/sph, Pb dep	2.11646	.87346	17.860
F31mar	Massif Central, South	Montagne Noire	Gal/diss. sph, small working	2.12486	.87402	17.860
F11pey	Massif Central, South	Montagne Noire	Sph, gal , several lodes	2.09706	.85333	18.340
F12 ss	Massif Central, South	Montagne Noire	Sph with very little gal	2.08410	.84862	18.430
F27vm	Massif Central, South	Montagne Noire	galena	2.12004	.87270	17.910
F91cp	Massif Central, South	Montagne Noire/Cavennes	Sphal, galena	2.07998	.84165	18.630
F10b lg	Massif Central, South	Montagne Noire/Cavennes	Small mine	2.09150	.85185	18.360

Inv. No.	Region	Site	Description	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
F2arg1	Massif Central, South	Montagne Noire/Cavennes	Galena with minor sph, qz, bar	2.09902	.85503	18.280
F2arg2	Massif Central, South	Montagne Noire/Cavennes	Galena with minor sph, qz, bar	2.09885	.85472	18.310
F3bley	Massif Central, South	Montagne Noire/Cavennes	Sphal, gal, bar	2.07746	.84239	18.590
F10mal	Massif Central, South	Montagne Noire/Cavennes	massive galena	2.09017	.85117	18.410
F6mil	Massif Central, South	Montagne Noire/Cavennes	Galena, small mine	2.09728	.85000	18.400
F4noz	Massif Central, South	Montagne Noire/Cavennes	Bar, qz, gal, sph, chalcop	2.08860	.84657	18.510
F4noz1	Massif Central, South	Montagne Noire/Cavennes	Bar, qz, gal, sph, chalcop	2.09042	.84732	18.470
F8tre1	Massif Central, South	Montagne Noire/Cavennes	Sphal, galena	2.08958	.84908	18.420
F8tre2	Massif Central, South	Montagne Noire/Cavennes	Sphal, galena	2.09185	.84946	18.400
F5via	Massif Central, South	Montagne Noire/Cavennes	Arsenopyrite, Ag, large vein	2.08002	.84103	18.620
F7vil1	Massif Central, South	Montagne Noire/Cavennes	Sphal, gal, chalcop, qz	2.09684	.85147	18.380
F7vil2	Massif Central, South	Montagne Noire/Cavennes	Sphal, gal, chalcop, qz	2.09224	.84916	18.430
F7vil3	Massif Central, South	Montagne Noire/Cavennes	Sphal, gal, chalcop, qz	2.09739	.85038	18.380
F18arg	Massif Central, South	Montagne Noire/Folat	Sph, gal, pyr, arsenop, bourno	2.09716	.85535	18.320
F20bar	Massif Central, South	Montagne Noire/Folat	Arsen, chalcop, gal, sph, sid	2.09012	.85071	18.420
F19bour1	Massif Central, South	Montagne Noire/Folat	Stibnite, arsenop	2.10466	.85863	18.250
F19bour2	Massif Central, South	Montagne Noire/Folat	Stibnite, arsenop	2.10417	.85855	18.240
F17fol	Massif Central, South	Montagne Noire/Folat	Various sulphides in veins	2.08760	.85092	18.380
F25cau	Massif Central, South	Montagne Noire/Folat	Sphal, Ag	2.09234	.85280	18.410
F16rab1	Massif Central, South	Montagne Noire/Folat	Gal, sph, pyr, arsenop	2.10175	.85722	18.280
F16rab2	Massif Central, South	Montagne Noire/Folat	Gal, sph, pyr, arsenop	2.10175	.85722	18.280
F16rab3	Massif Central, South	Montagne Noire/Folat	Gal, sph, pyr, arsenop	2.10186	.85706	18.260
F23lac	Massif Central, South	Montagne Noire/Folat	Pyr, sid with sph, gal	2.09027	.84649	18.500
F26las	Massif Central, South	Montagne Noire/Folat	gal, small vein	2.09096	.85349	18.360
F22prad	Massif Central, South	Montagne Noire/Folat	Gal, qz, small prospect	2.09205	.85185	18.360
F21olar	Massif Central, South	Montagne Noire/Folat	Arsen, chalcop, gal, sph, sid	2.08963	.85062	18.410
F34 stj	Massif Central, South	Montagne Noire/Vivarais	Gal, sph, chalcop, small work	2.07481	.84177	18.580
F1fig1	Massif Central, South	Western edge of MC	Sphalerite, calcite, minor gal	2.08028	.84159	18.560
F1fig2	Massif Central, South	Western edge of MC	Sphalerite, calcite, minor gal	2.08032	.84313	18.550
BW 333 oxf	Schwarzwald	Arzberg	Galena	2.07396	.83629	18.694
GER 73 B	Schwarzwald	Brandenburg	Ga finr gr. with qz	2.08030	.83919	18.668

Inv. No.	Region	Site	Description	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb
BW 356 oxf	Schwarzwald	Nussloch	Galena	2.07192	.83656	18.661
GER 93 B	Schwarzwald	Schappach	Ga with py, calc	2.08307	.84334	18.563
GER 100 B	Schwarzwald	Schauinsland	Ga with sph, chalc, qz	2.07716	.84261	18.584
GER 95 B	Schwarzwald	Schauinsland	Ga brecciated	2.08404	.84527	18.516
BW 473 oxf	Schwarzwald	Teufelsgrund/Bresgau	Galena	2.08207	.84391	18.526
BW 496 oxf	Schwarzwald	Wolfach	Galena	2.08269	.84388	18.492
Schwarz 9a oxf	Schwarzwald, Badenweiler	Friedrichsruhe	Galena, Pb/Ag ore	2.06581	.83653	18.656
Oe 11 oxf	Tyrol	Kitzbuhel	Chalcopyrite	2.06411	.83224	18.806
OLK 1A	South Poland	Olkusz	Galena	2.08583	.84799	18.442
OLK 1B	South Poland	Olkusz	Galena	2.08822	.84864	18.449
OLK 2A	South Poland	Olkusz	Galena	2.08736	.84849	18.445
OLK 2B	South Poland	Olkusz	Galena	2.08529	.84809	18.426
OLK 2C	South Poland	Olkusz	Galena	2.08517	.84828	18.415
OLK 3A	South Poland	Olkusz	Galena	2.08736	.84821	18.443
OLK 3B	South Poland	Olkusz	Galena	2.08799	.84883	18.443
OLK 3C	South Poland	Olkusz	Galena	2.08846	.84841	18.468
OLK 4A	South Poland	Olkusz	Galena	2.08824	.84820	18.478
OLK 5A	South Poland	Olkusz	Galena	2.08984	.84879	18.495
OLK 5B	South Poland	Olkusz	Galena	2.08798	.84836	18.474
OLK 5C	South Poland	Olkusz	Galena	2.08987	.84873	18.488