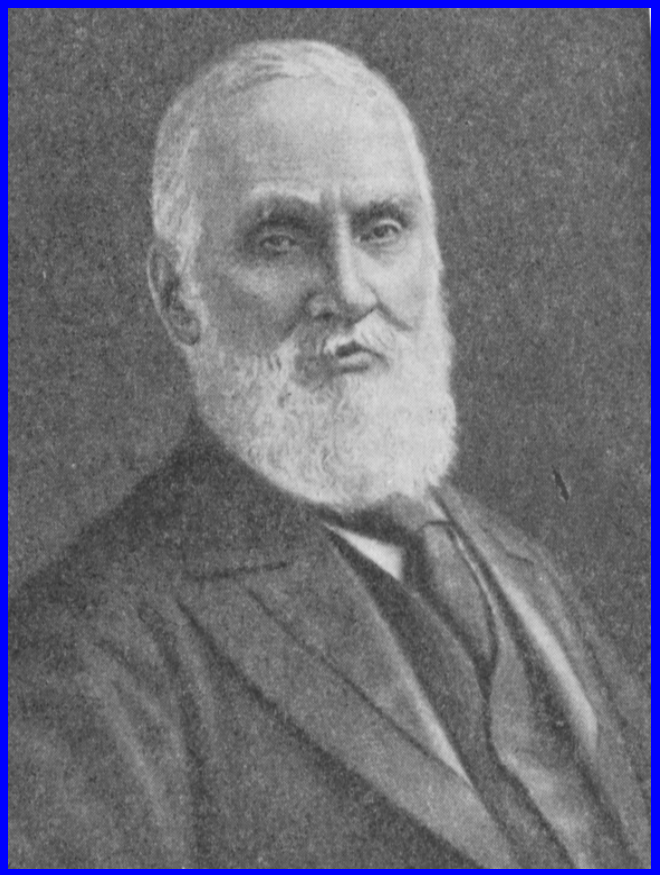
ARCHAEOMETRY: THE FIELD FOR APPLICATION OF CHEMICAL ANALYSIS

Prof. Dr. Ivelin Kuleff, DSc

Faculty of Chemistry,
St. K. Ohridski University of Sofia
BULGARIA



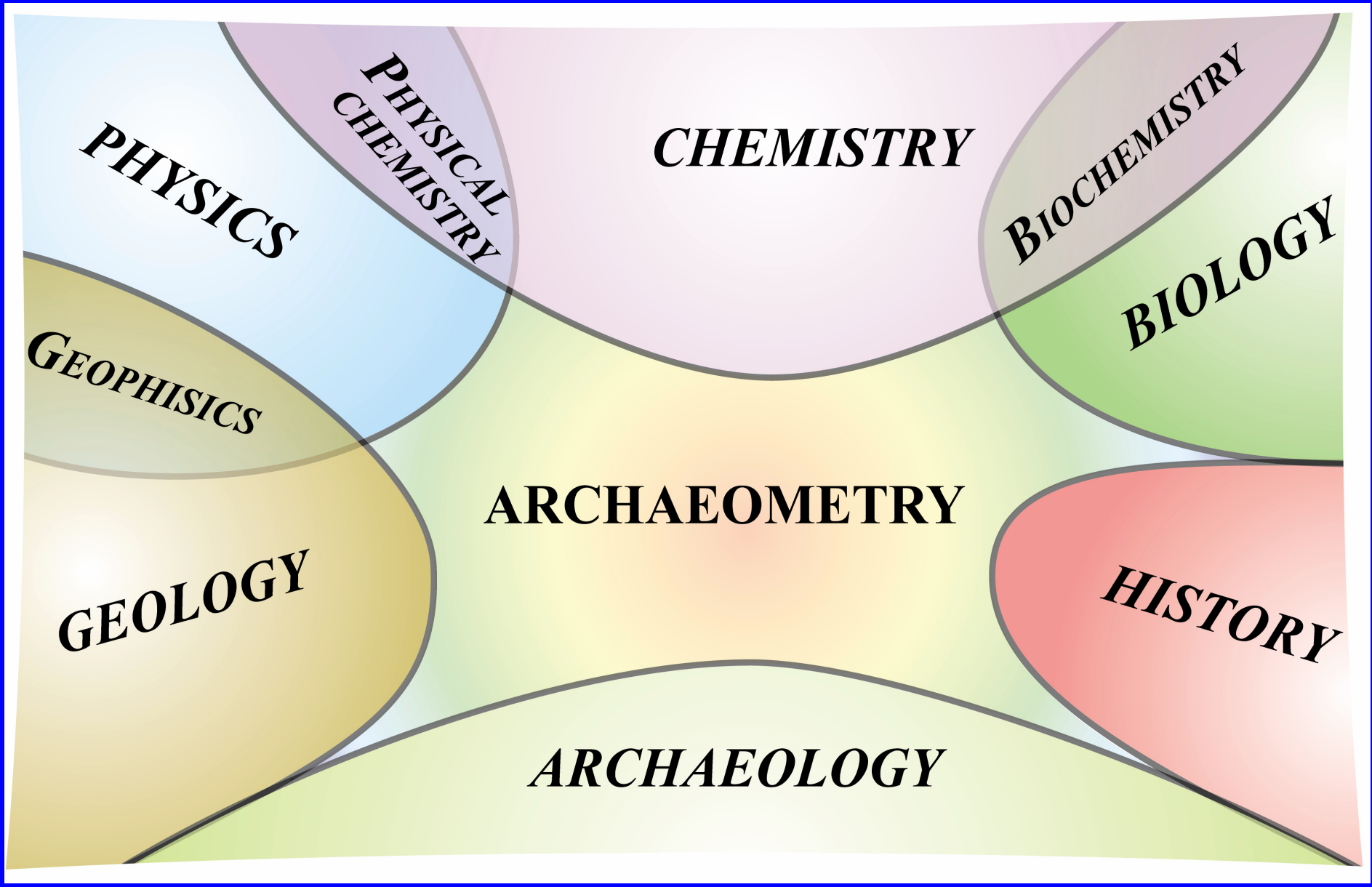
Thomson William
Lord Kelvin (1824–1907)

“I often say that when you can measure what you are speaking about and express it in numbers you know something about it, but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind”

Lord Kelvin, 1883

„Често казвам, че когато можете да измерите онова, за което говорите и го представите в числа, тогава знаете нещо за него, но когато не можете – Вашите познания са оскъдни и незадоволителни“

Лорд Келвин, 1883 г.



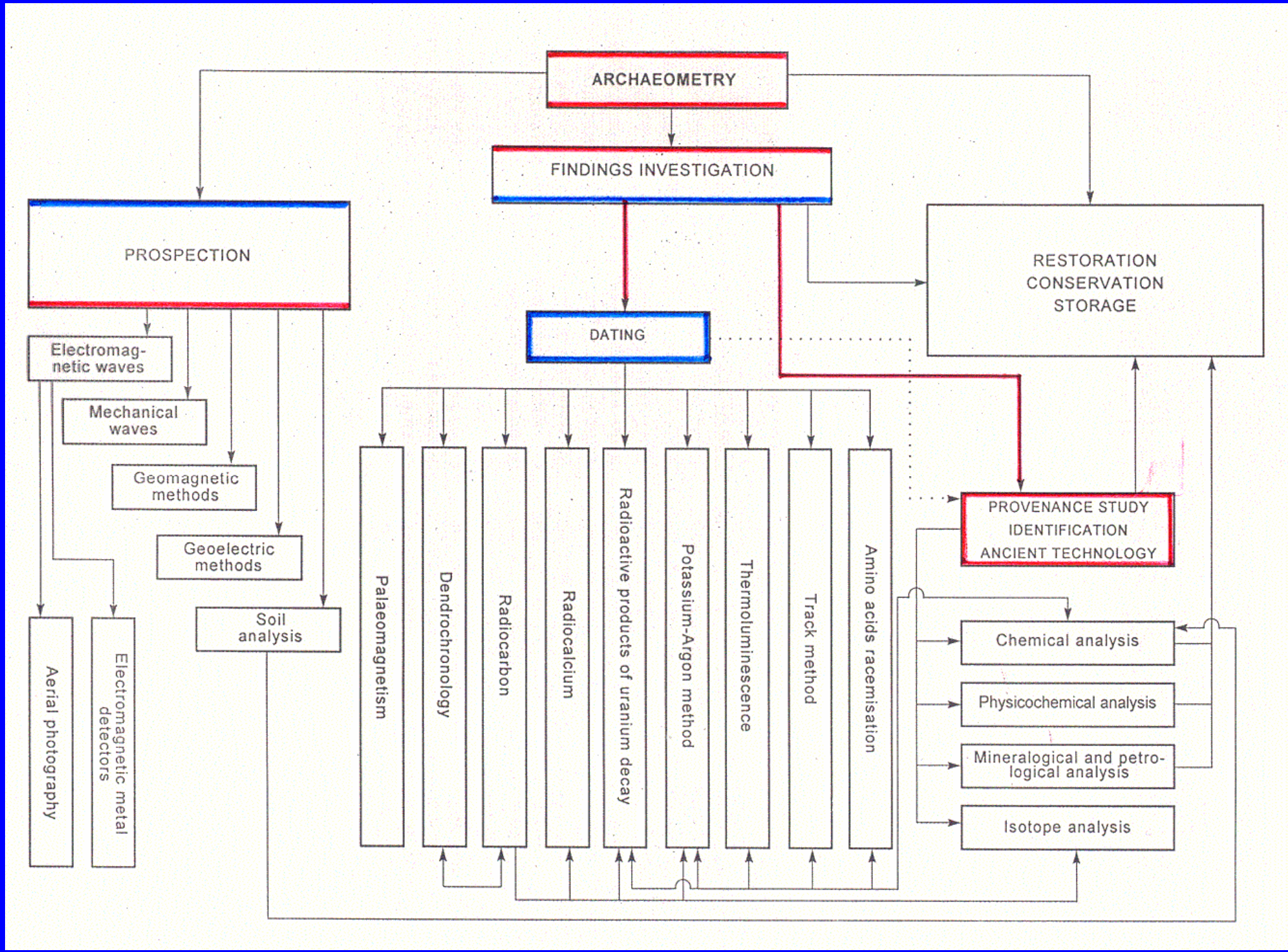
The place of archaeometry among different sciences and humanitarian disciplines

Kuleff & Djingova, Anal. Lab. 5 (1996) 75

Archaeometry covers the application of modern physical and chemical methods in the investigation of archaeological materials with the aim to solve historical and archaeological problems.

The term "archaeometry" indicates that the archaeological finds are to be measured and quantified.

The term "archaeometry" describes emphasis on dating, quantification, and physicochemical analysis of archaeological materials.


ARCHAEOMETRY
FINDINGS INVESTIGATION
PROSPECTION
RESTORATION
CONSERVATION
STORAGE
DATING
Electromag-
netic waves
Mechanical
waves
Geomagnetic
methods
Geoelectric
methods
Soil
analysis
Aerial photography
Electromagnetic metal
detectors
Palaeomagnetism
Dendrochronology
Radiocarbon
Radiocalcium
Radioactive products of uranium decay
Potassium-Argon method
Thermoluminescence
Track method
Amino acids racemisation
PROVENANCE STUDY
IDENTIFICATION
ANCIENT TECHNOLOGY
Chemical analysis
Physicochemical analysis
Mineralogical and petro-
logical analysis
Isotope analysis

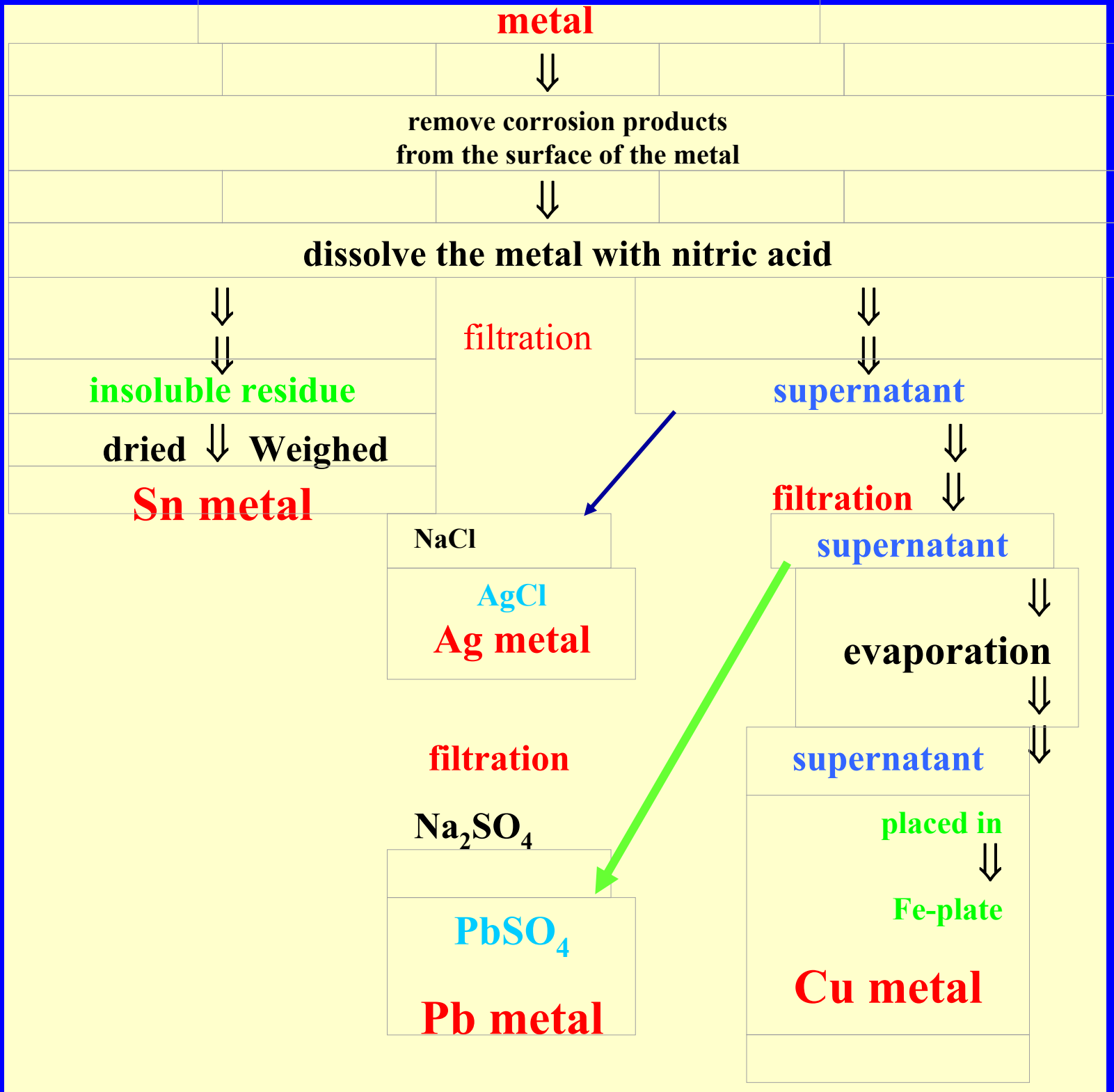
Martin-Heinrich Klaprot
(1743–1818)
German chemist and pharmacist

Klaproth determined the composition of Greek and Roman coins, a number of other metal objects as well as few pieces of differently colored Roman glass.

The aim of this analysis was to determine the chemical composition of ancient materials and to evaluate the technology used by ancient craftsmen.

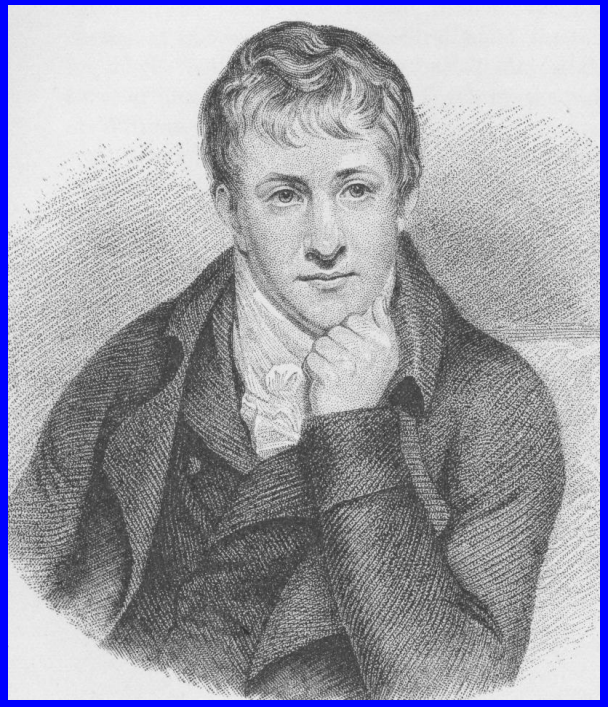
Discoverer of the chemical elements uranium, zirconium, and cerium as well as founder of analytical chemistry

The method of analysis of bronze developed by Klaprot



Thus, starting from the first archaeometric investigations, contributions are presented, which can be achieved in archaeometric studies:

1. **development of the analytical methods of analysis**
2. **receiving new facts for archaeology and history**



Сър Хъмфри Дейви
(Humphery Davy)
(1778–1829)

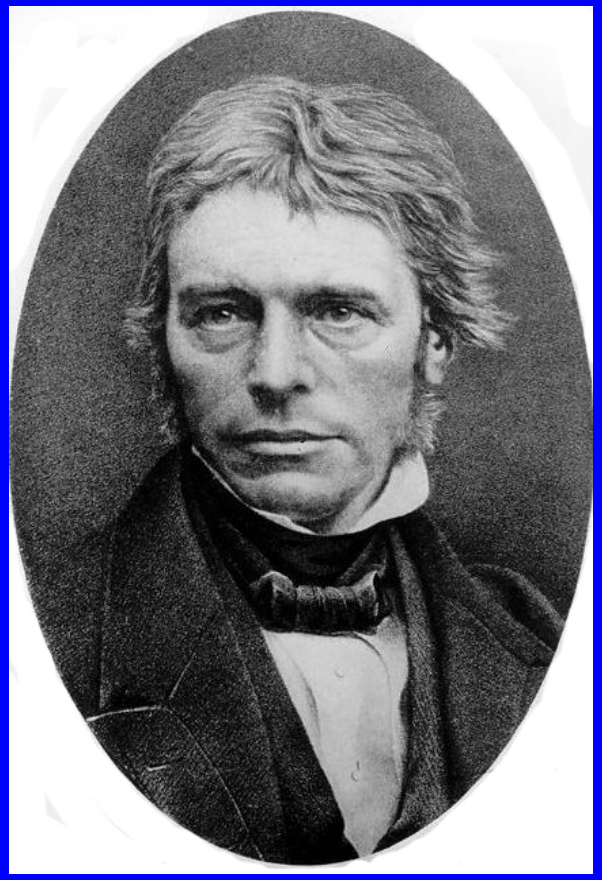
Creator of the electrochemical theory of the structure of the materials. He proposed electrolysis as a method for recovery of alkali and alkaline metals. Discoverer of the chemical element boron. Creator of the safe mining lamp that preserves from choke-damp.

In 1815, Davy carried out analyses of ancient pigments collected at Rome and Pompeii. He confirmed the evidence for natural pigments and identified a synthetic pigment called “Egyptian Blue” formed by fusing copper, silica and sodium carbonate.

Йенс Якоб Берцелиус (J. J. Berzelius) (1779–1848)

One of the founders of modern chemistry.

Berzelius was interested in the composition of ancient bronzes



Майкъл Фарадей
(M. Faraday)
(1791–1867)

The creator of the theory of electromagnetism.

One of the founders of electrochemistry.

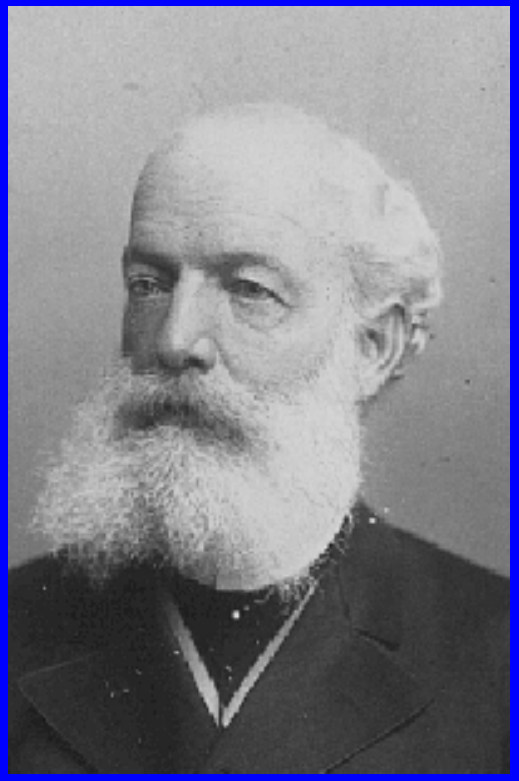
Faradey studied a Roman pottery glaze and provided indications on chemical grounds of the use of lead glaze in antiquity.

Марсел Бертло
(Marcelin Barthelot)
(1827–1907)

The founder of thermochemistry.
He carried out the first analysis of natural organic materials.

Berthelot investigated corrosion products of metals and changes of organic materials with time

Berthelot investigated some 150 artefacts from Egypt and the Near East and might have less been interested in the exact composition of ancient materials than in obtaining results of immediate practical value to archaeology

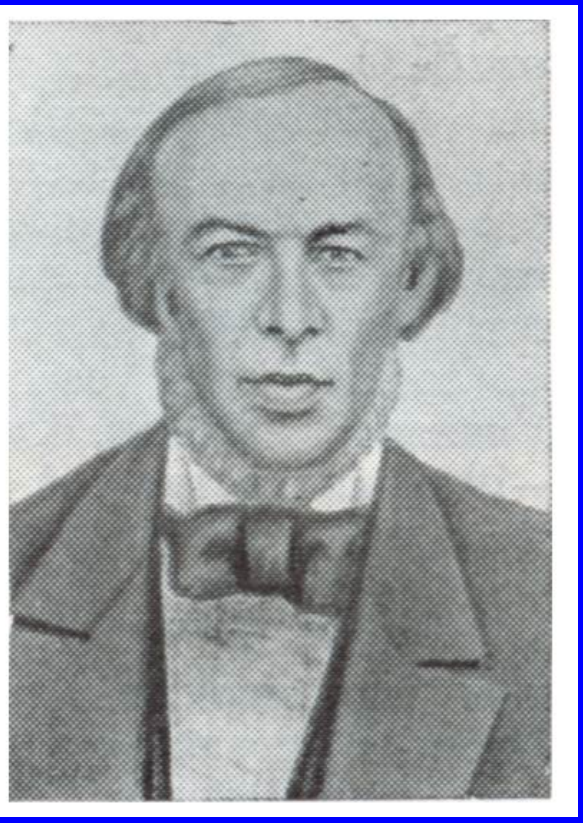


Аугуст Кекуле
(A. Kekule von Stradonitz)
(1829–1896)

One of the significant contributors to modern organic chemistry.

He established the structure of benzene.

Kekule carried out analyses of ancient samples of wood tar and proved that the tar is composed of aromatic compounds



Карл Фрезениус
(K. Fresenius)
(1818–1897)

Fresenius organized a chemical laboratory at the Institute of Agriculture in Wiesbaden (Germany) which in the middle of the 19th century had the reputation of the best analytical laboratory in Europe.

The author of the classic handbook on qualitative and quantitave analysis. This textbook was used by many generations of chemists.

Fresenius carried out a large number of analyses of ancient objects: metals and alloys.

Уилърд Либи
(W. F. Libby)
(1908–1980)

Significant contribution to the natural radioactivity of light elements: first measurements of the radioactive isotope of carbon (^{14}C). Development of counter for measurement of radiocarbon.

"Seldom has a single discovery in chemistry had such an impact on the thinking in so many fields of human endeavor. Seldom has a single discovery generated such wide public interest"
Prof. Westgren

Libby proposed a method of establishing absolute chronology throughout the world using the determination of the radioactivity of carbon-14.

What has been made in Bulgaria in the field of archaeometry?

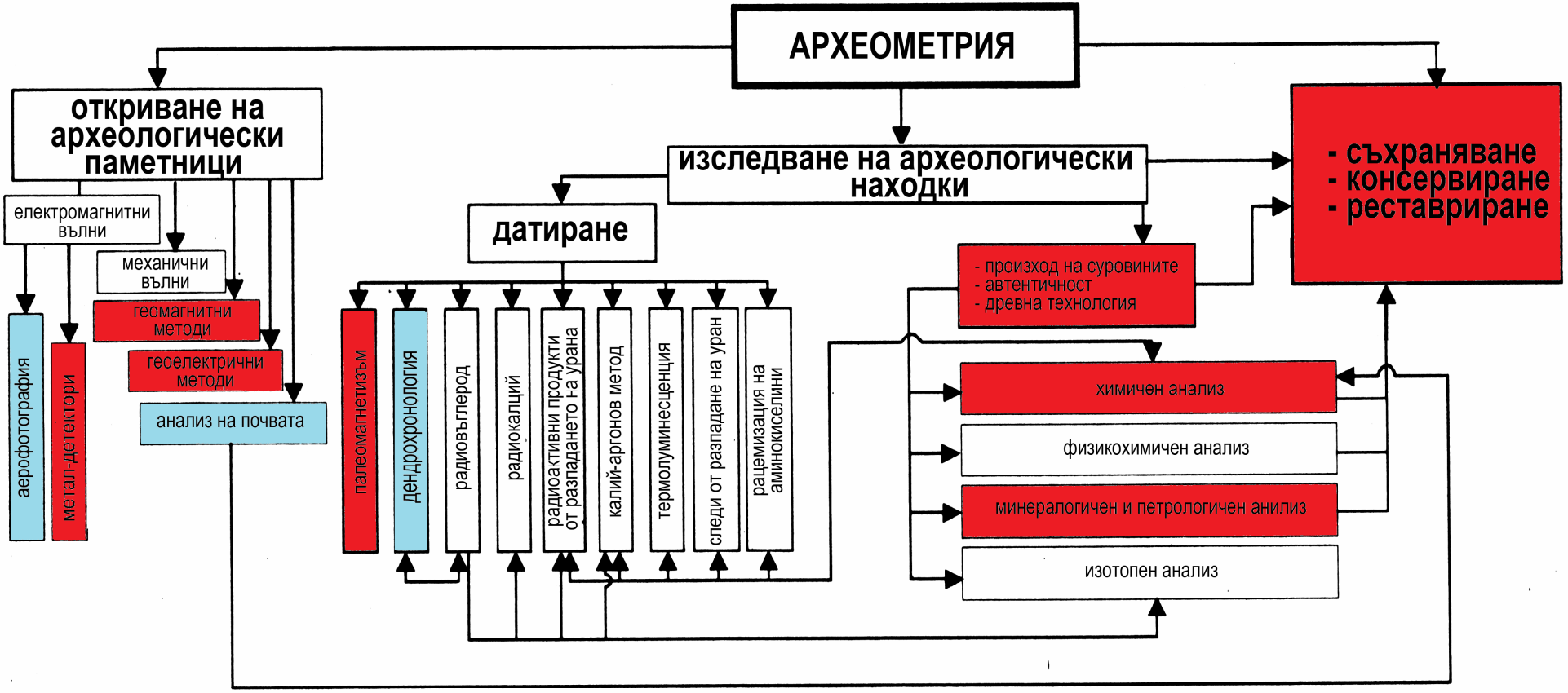
By the end of the 19th century the first Bulgarian works in the field of archaeometry were published. They reported on mining activity and metallurgy in Bulgaria.

At the end of the 50's and the beginning of the 60's, Bulgarian works reporting the chemical concentration of archaeological finds were published.

The works of the Russian Bezborodov and the Bulgarian Marin Marinov, later head of the Chair of Silicates at the former Chemical-Technological Institute in Sofia, involve basic investigations in the field of archaeometric studies of glasses.

Investigations of metal objects by metallographical study at the University of Sofia were carried out by Prof. Trifonoff and co-workers.

What has been made in Bulgaria in the field of archaeometry?



Red: fields in which scientists have worked and are working in Bulgaria

Blue: fields in which some achievements have been made in Bulgaria

What kind of archaeological materials have been investigated by the methods of archaeometry in Bulgaria?

1) Pottery: Sofia University
2) Glass: Sofia University, University of Chemical Technology and Metallurgy, Bulgarian Academy of Sciences
3) Amber: Sofia University
4) Bone: Sofia University, Bulgarian Academy of Sciences
5) Metals: Sofia University, National Institute of Archaeology and Museum
   - 5.1) copper and copper-based alloys (bronze; brass)
   - 5.2) lead
   - 5.3) gold
   - 5.4) iron
6) Rocks and minerals: University of Mining and Geology
7) Pigments: National Academy of Arts, Sofia University

INVESTIGATIONS OF THE FINDS

More than 25% of all archaeometric investigations are provenance studies.

Over 50% of the provenance studies are provenance studies of archaeological pottery finds.

Provenance studies are generally based on the fact that the chemical composition of an artefact usually reflects the geochemical features of the raw materials it was made of.

The chemical composition of ceramic finds reflects very accurately the geochemical characteristics of the region where the clay for their production came from.

The clay source is generally identified with the place of pottery production.

This assumption is based on the information that in 85% of the cases the clay used for pottery production was obtained within 7 km of the respective workshop.

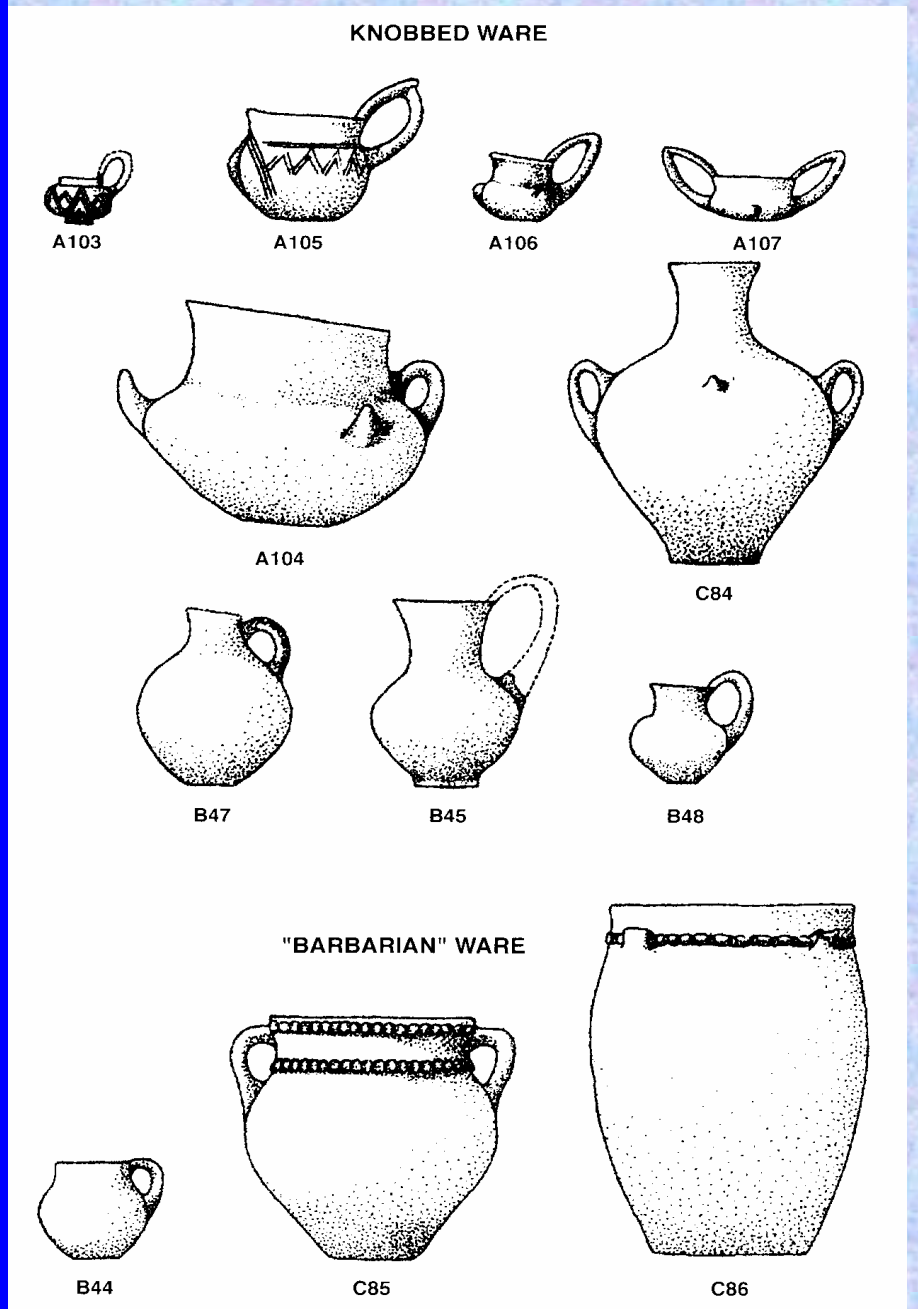
In very rare cases the distance may extend as much as 50 km from the manufacturing location.

The Origin of Course Wares of Troia VII

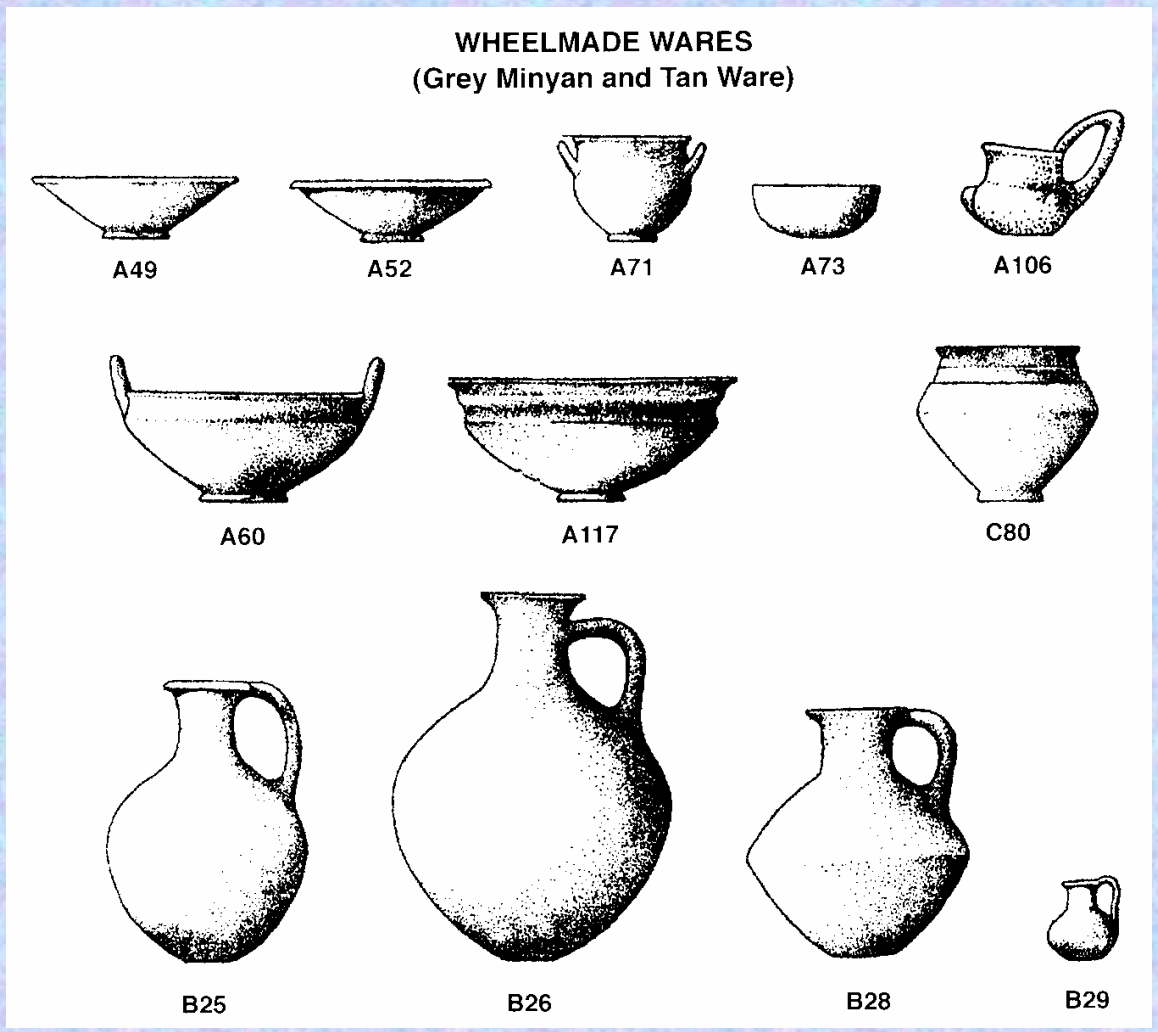
Question: Some peoples, "barbarians", immigrated to Northwestern Anatolia in the period following the destruction of Troia by the end of Bronze Age

"Barbarian"-type vessels appeared in the levels following the destruction of Troia VIIa period and continued through the entire VIIb period.

The beginning of Troia VIIb$_1$ and appearance of the "Barbarian" ware can be placed ca. 1200 BC

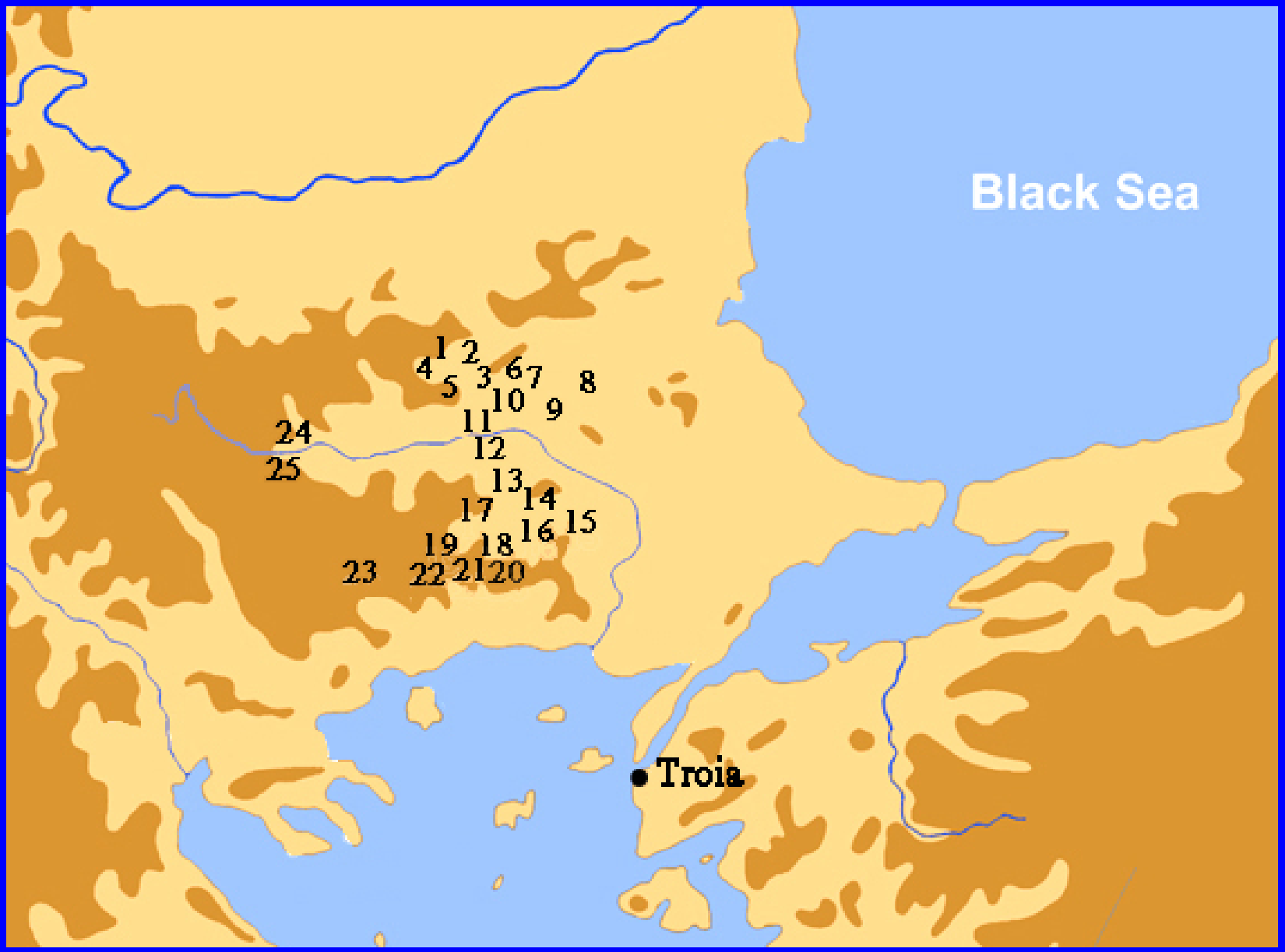


Pottery from House 768 in Troia



Traditional Troian wheel-made pottery:
Gray Minyan, Tan and Plain ware

Pottery from Thracia analyzed in this study



Map presenting the archaeological sites from which the investigated pottery come from

Using INAA the content of 24 chemical elements:

As, Au, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd,

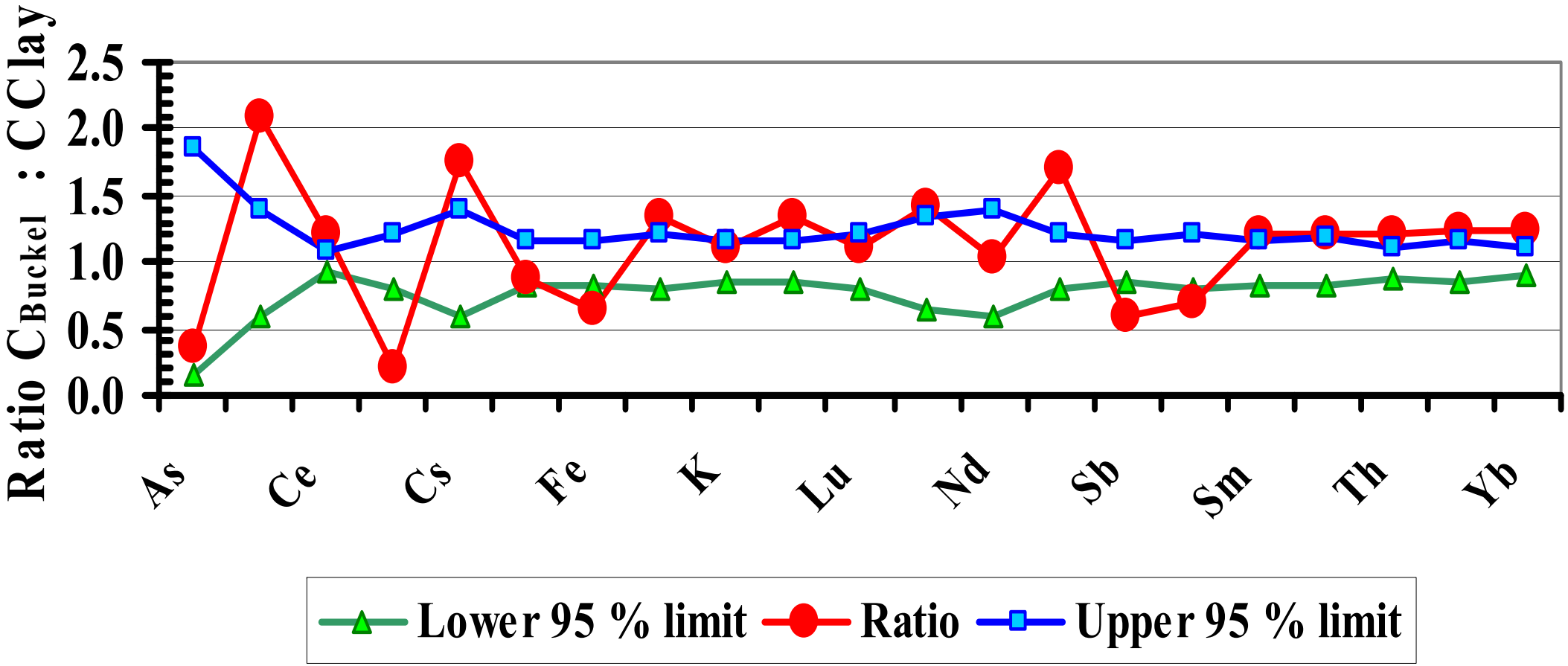
Rb, Sb, Sc, Sm, Ta, Tb, Th, U, and Yb

were determined in 43 ceramic shards, excavated in Troia, and 299 shards, excavated in Thracia (Southeastern Bulgaria).

The investigated ceramic sherds from Troia were grouped by cluster analysis based on similarity in the chemical composition: three clusters are formed.

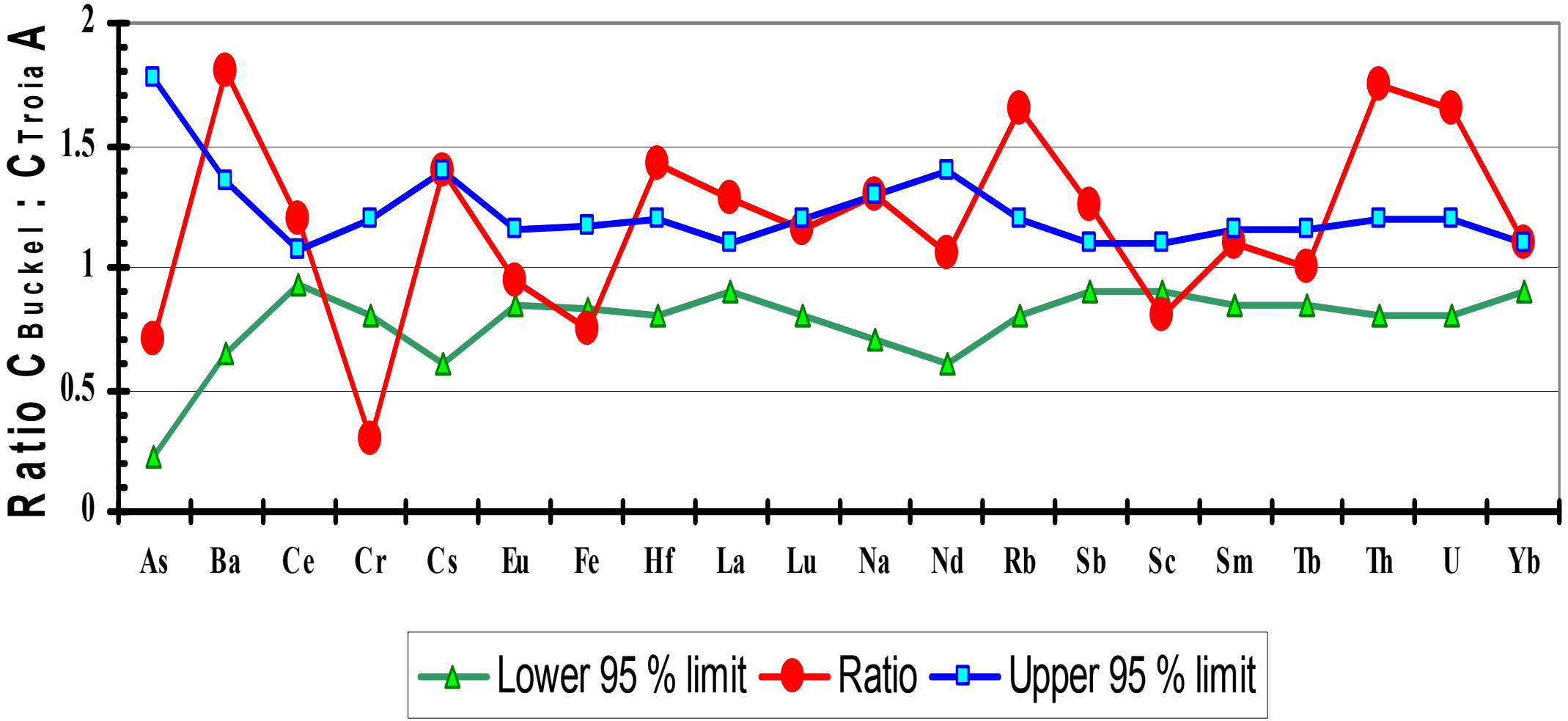
The chemical profile of the Troia pottery was compared with the profile of the local sediments from the Troian plain.

Buckelpottery from Troia *vs.* clay source Troia A



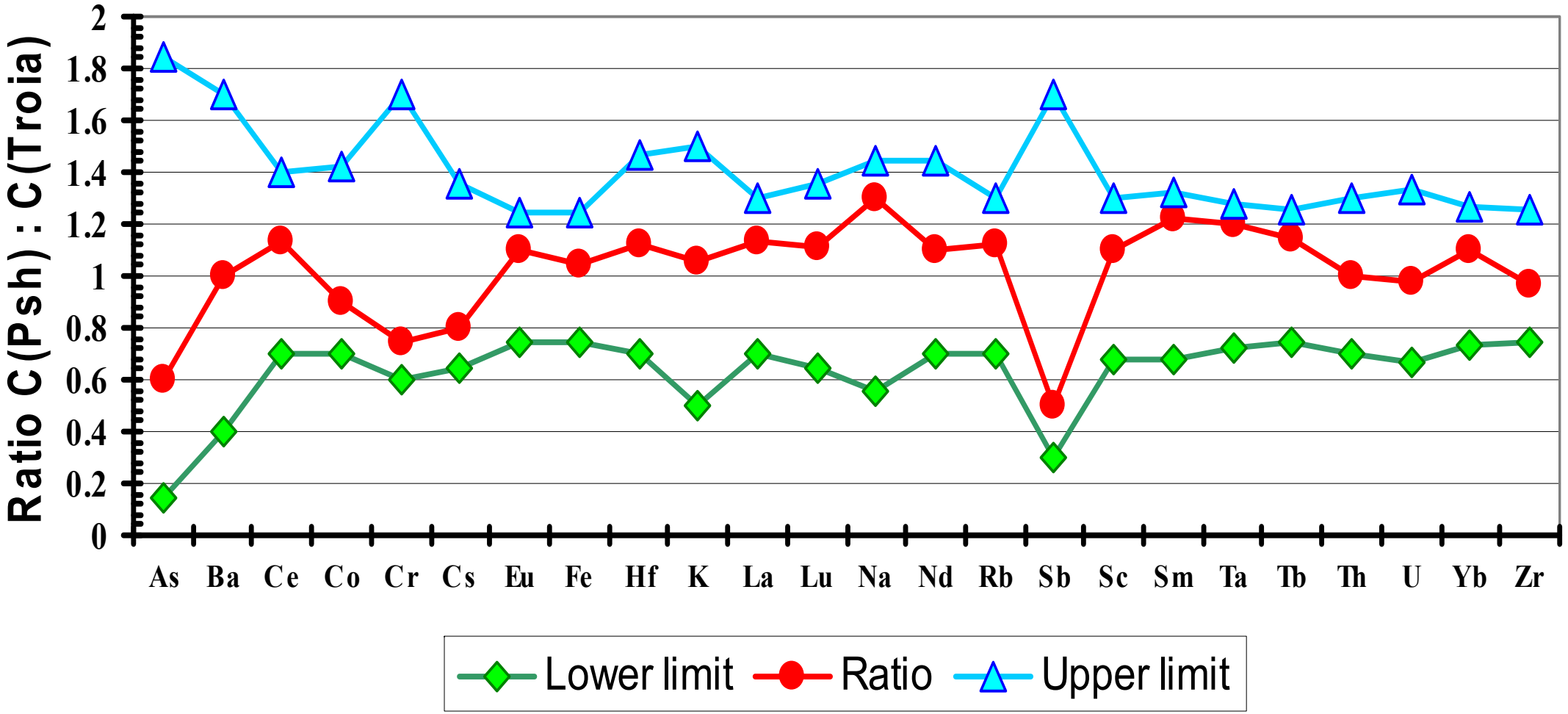
Comparison between the elemental composition of Buckelpottery excavated in Troia and clay source Troia A

The concentration of 11 elements is outside the 95% interval

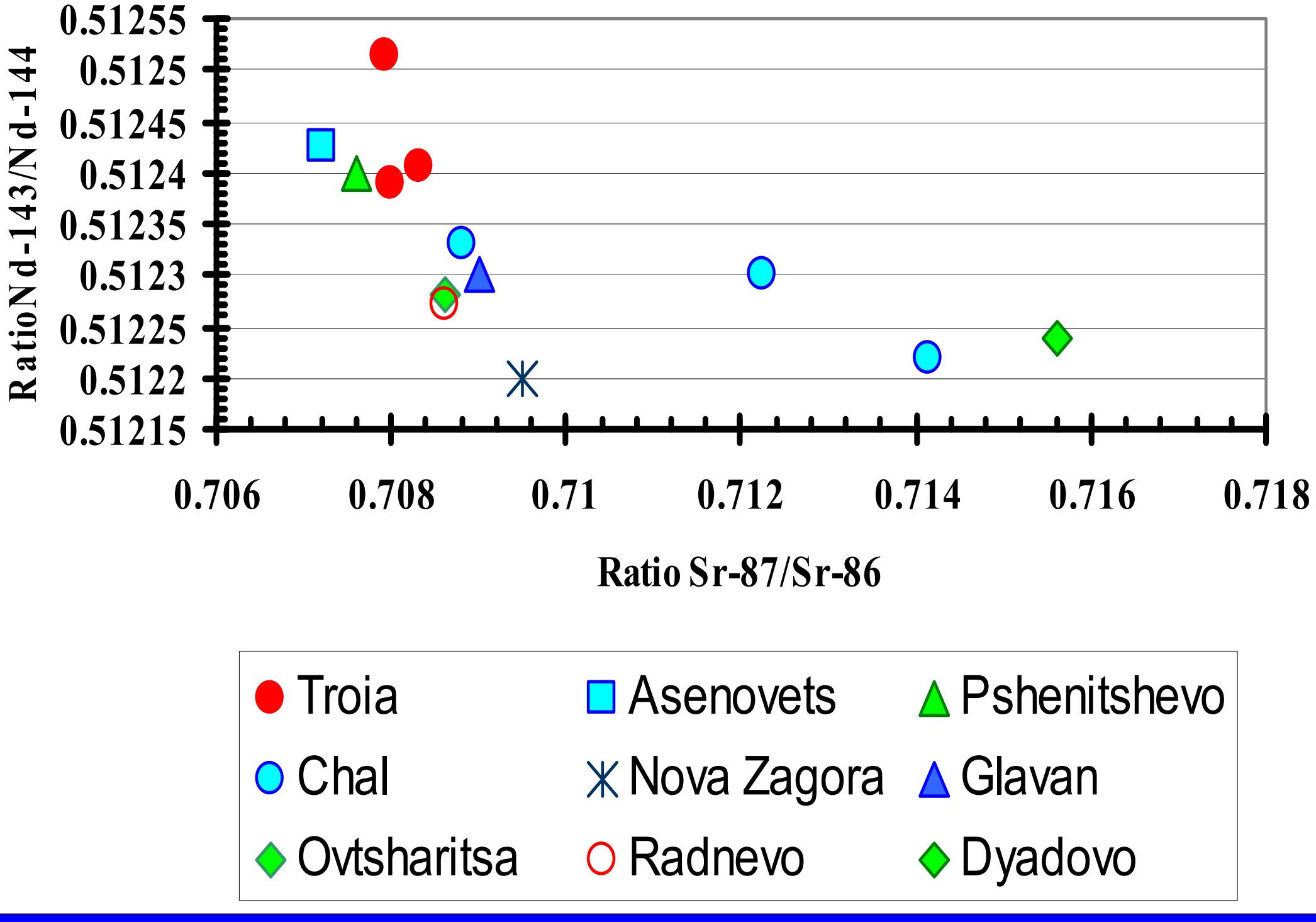


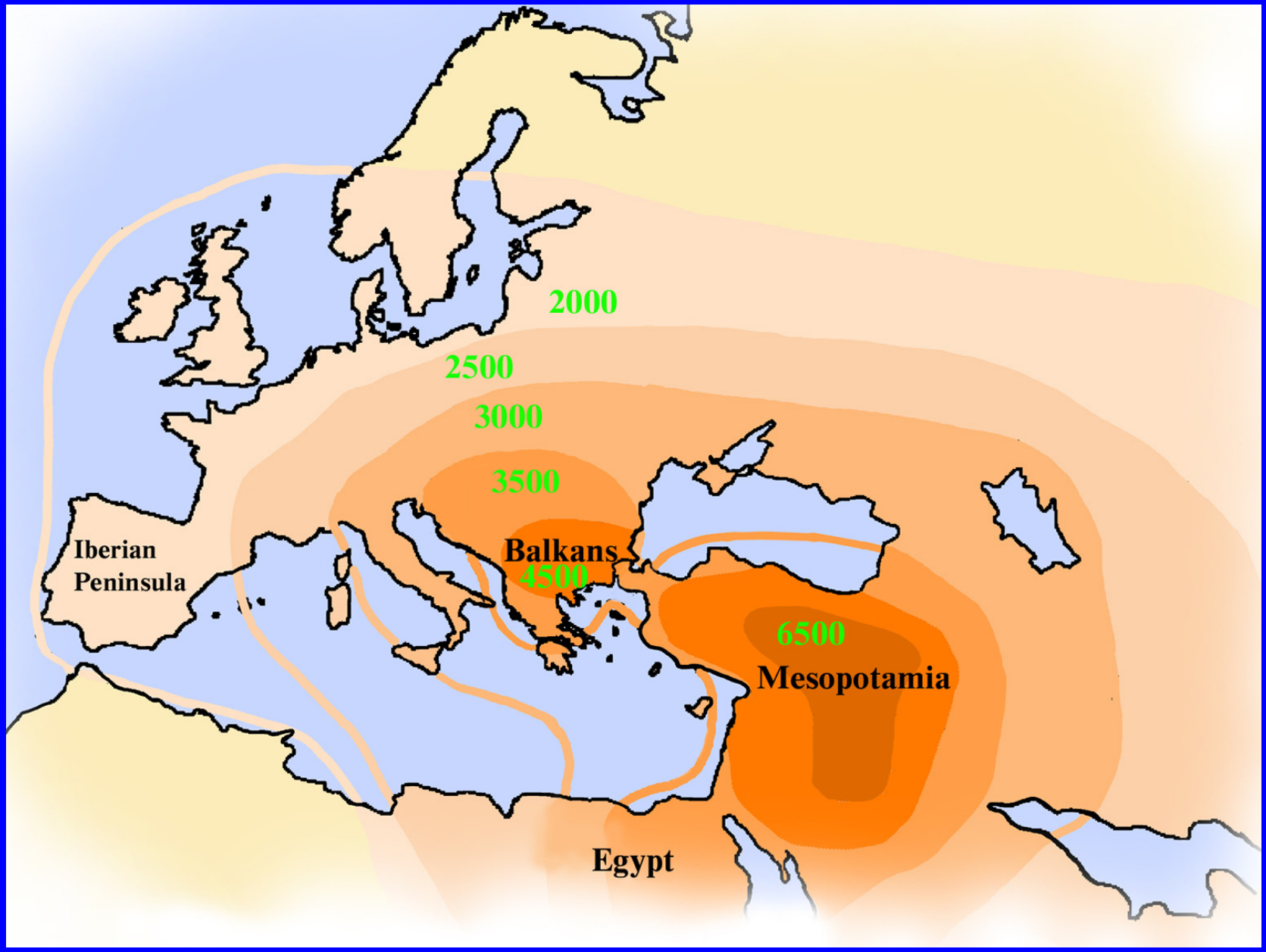
Comparison between the elemental composition of Buckelpottery excavated in Pshenichevo and clay source Troia A

The concentration of 11 elements is outside the 95% interval



Comparison between the elemental composition of pottery excavated in village Pshenichevo (Thracia) and Buckelceramic from Troia


0.51255
0.5125
0.51245
0.5124
0.51235
0.5123
0.51225
0.5122
0.51215
RatioNd-143/Nd-144
0.706
0.708
0.71
0.712
0.714
0.716
0.718
Ratio Sr-87/Sr-86
Troia
Asenovets
Pshenitshevo
Chal
Nova Zagora
Glavan
Ovtsharitsa
Radnevo
Dyadovo



Geographical distribution of metallurgy in Eurasia

6500–2000 BC

Map of Bulgaria with position of Varna

In the autumn of 1972, during industrial excavation works at the Varna Lake coast, the 20th century archaeological discovery of European prehistory was made. Archaeological excavations carried out during 1978–1992 discovered 298 unveiled burials.

Picture of burial No. 43

Some of the finds in the Chalcolithic necropolis of Varna which are dated to 4600–4430 BC

[Higham et al., 2007]

Besides ceramics, coppers and other objects in the excavated 298 graves, being an exclusive interest for scientific investigation of the prehistoric society, also a variety of gold finds was found. The number of gold finds is above 3000 with total weight of more than 6 kg!

The aim of this first truly comprehensive study of the Varna necropolis golden object investigation is to characterize chemically the gold finds and to discover gold origin.

Using energy dispersive X-ray fluorescence (ED-XRF) with portable Bruker Tracer III-V instrument the concentration of gold, silver and copper has been determined.

All golden artefacts from Halcolithic necropolis of Varna (~ 3120 artefacts) have been analyzed. Using XRF it was possible to determine the concentration of Ag, Au, and Cu.

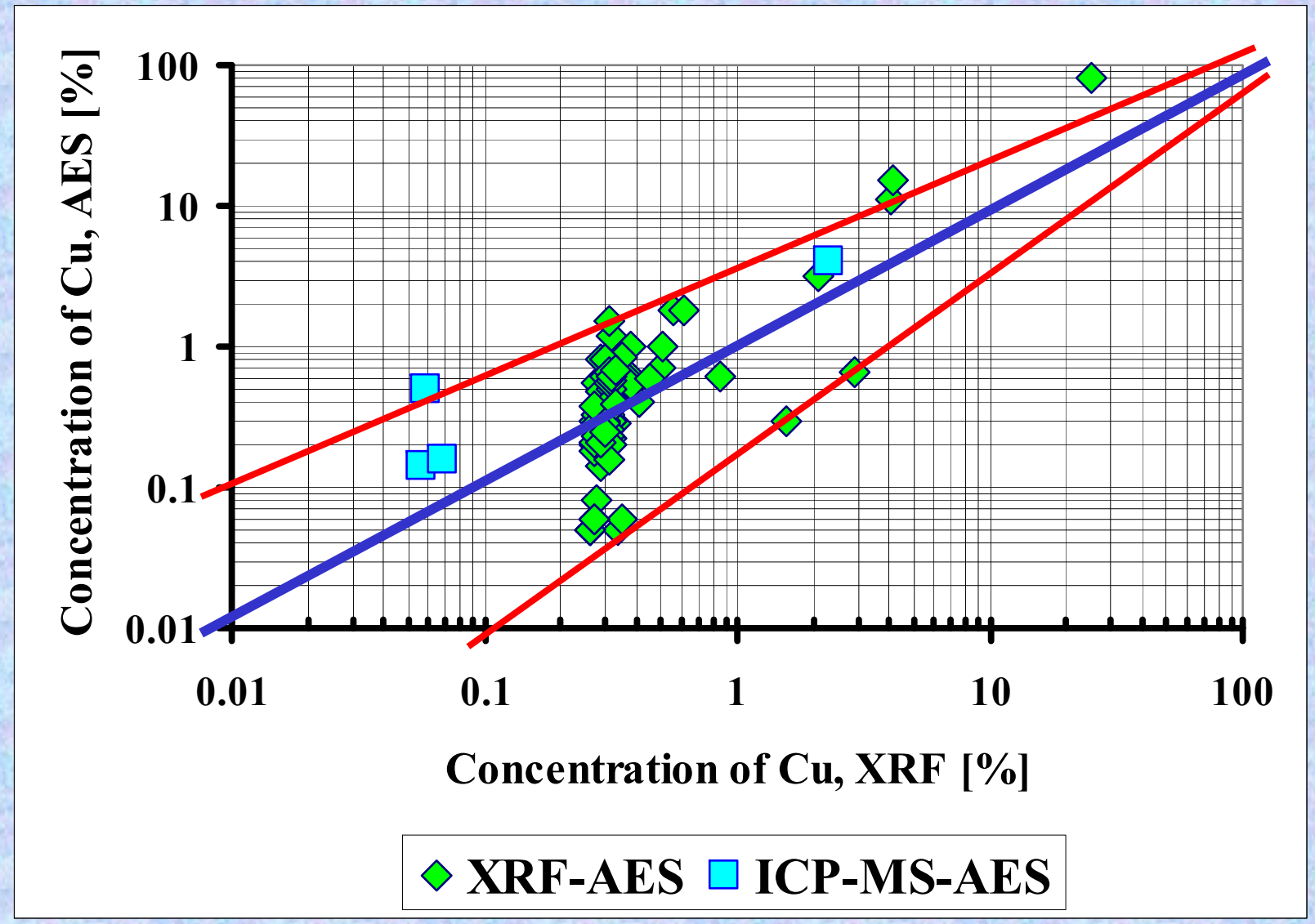
At the same time geological expedition gathered more than 100 samples from some of the river sediments in Eastern Bulgaria

Element	Certificate values	Our values	RSD [%]	Absolute difference	SR [%]
Cu	13.0	11.3±0.1	0.96	–1.7	13.1
Ag	22.9	24.7±0.1	0.44	+1.8	11.7
Au	59.3	57.7±0.1	0.19	–1.8	3.3

M = mean value
SD = standard deviation
RSD = relative standard deviation

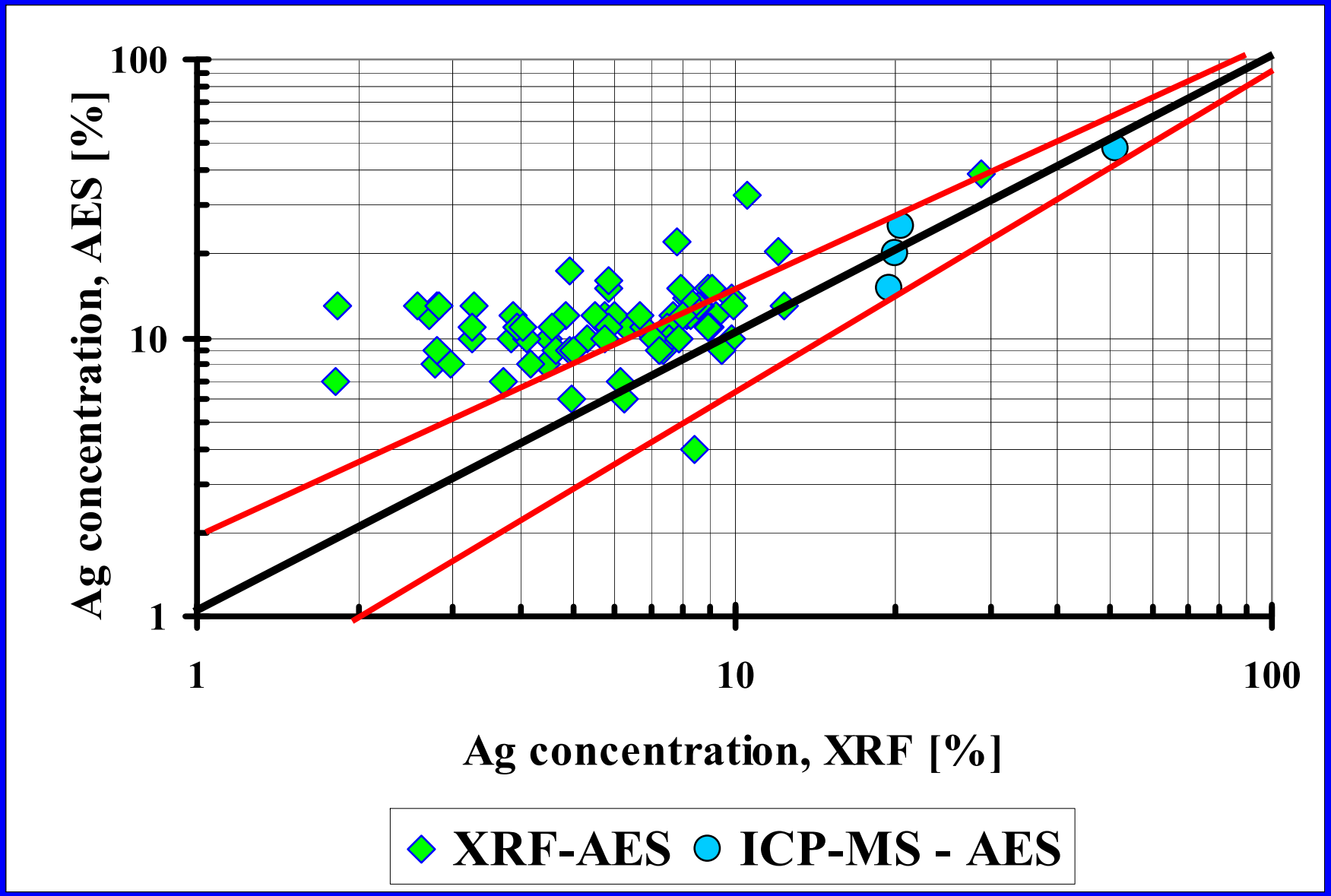
$$SR = \frac{\left| C_{\exp} - C_{st} \right| + 2SD}{C_{st}} 100$$

[MacFarren et al. (1970)]
SR < 25 %: **excellent coincidence**;
25 % < SR < 50 %: good coincidence;
SR > 50 %: poor coincidence.



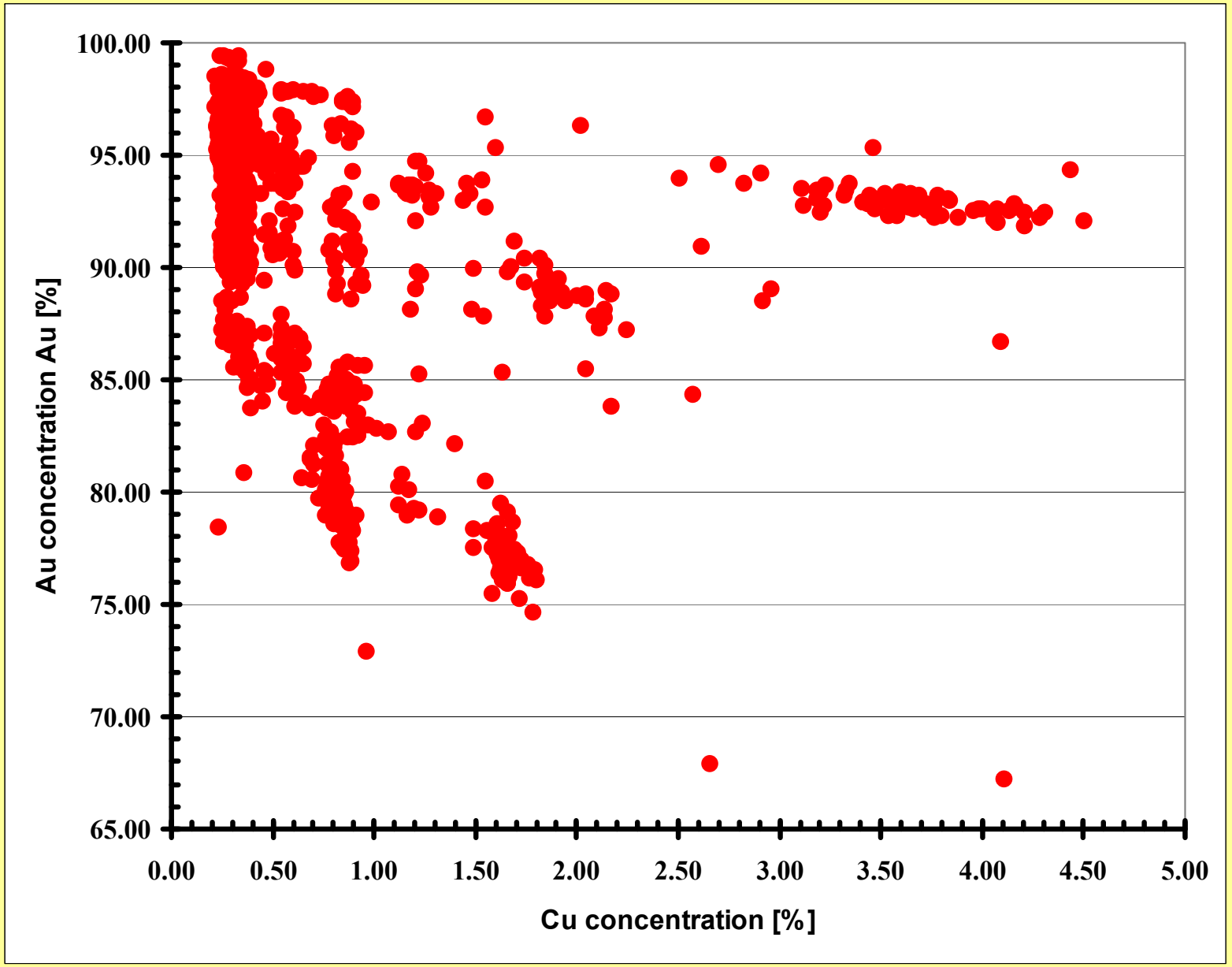
Comparison between results of copper concentration obtained by Hartmann using classical AES and this study using ED-XRF

Hartmann, Studia Prehistorica, 1/2 (1978) 27

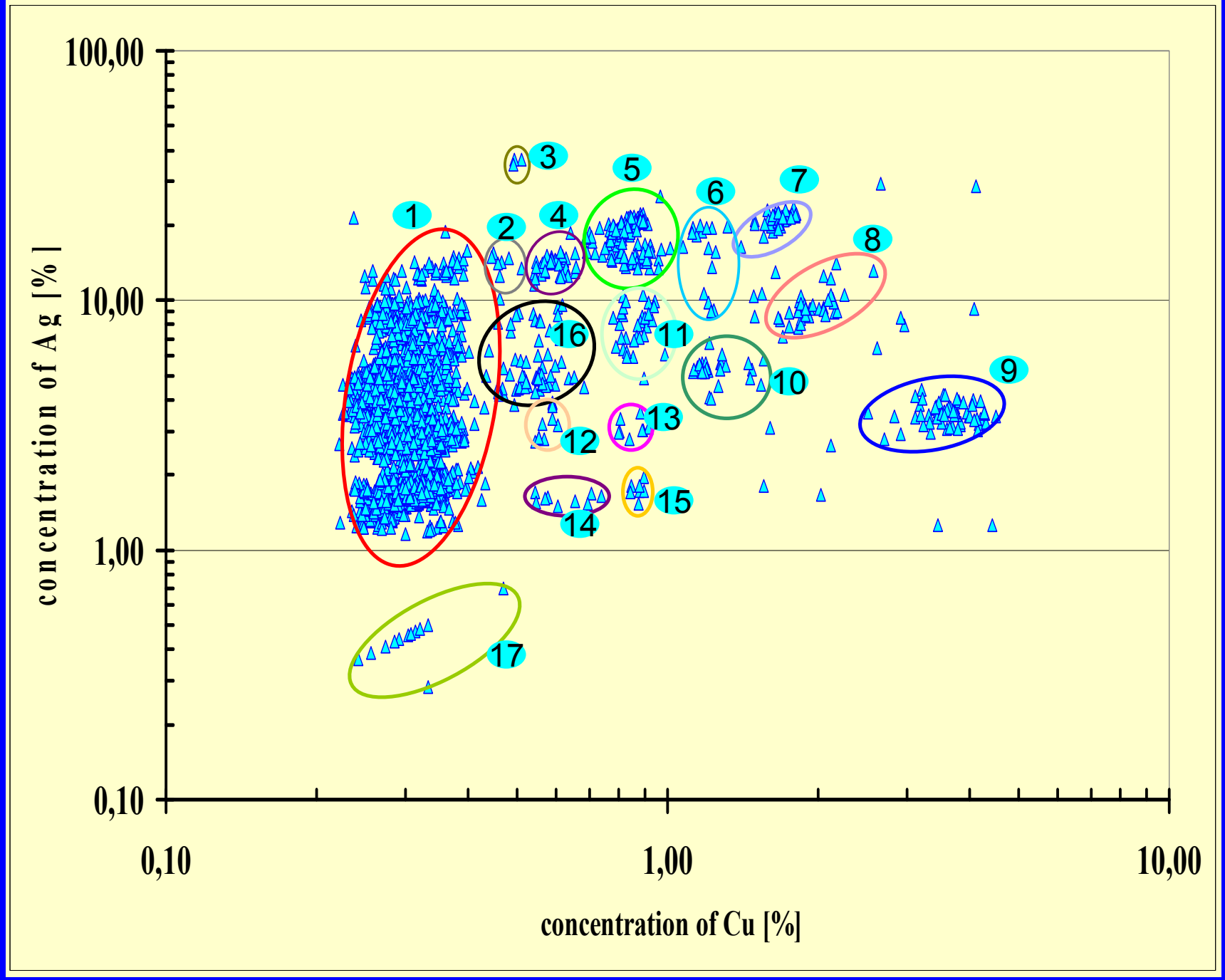


Comparison between results of silver concentration obtained by Hartmann using classical AES and this study using ED-XRF

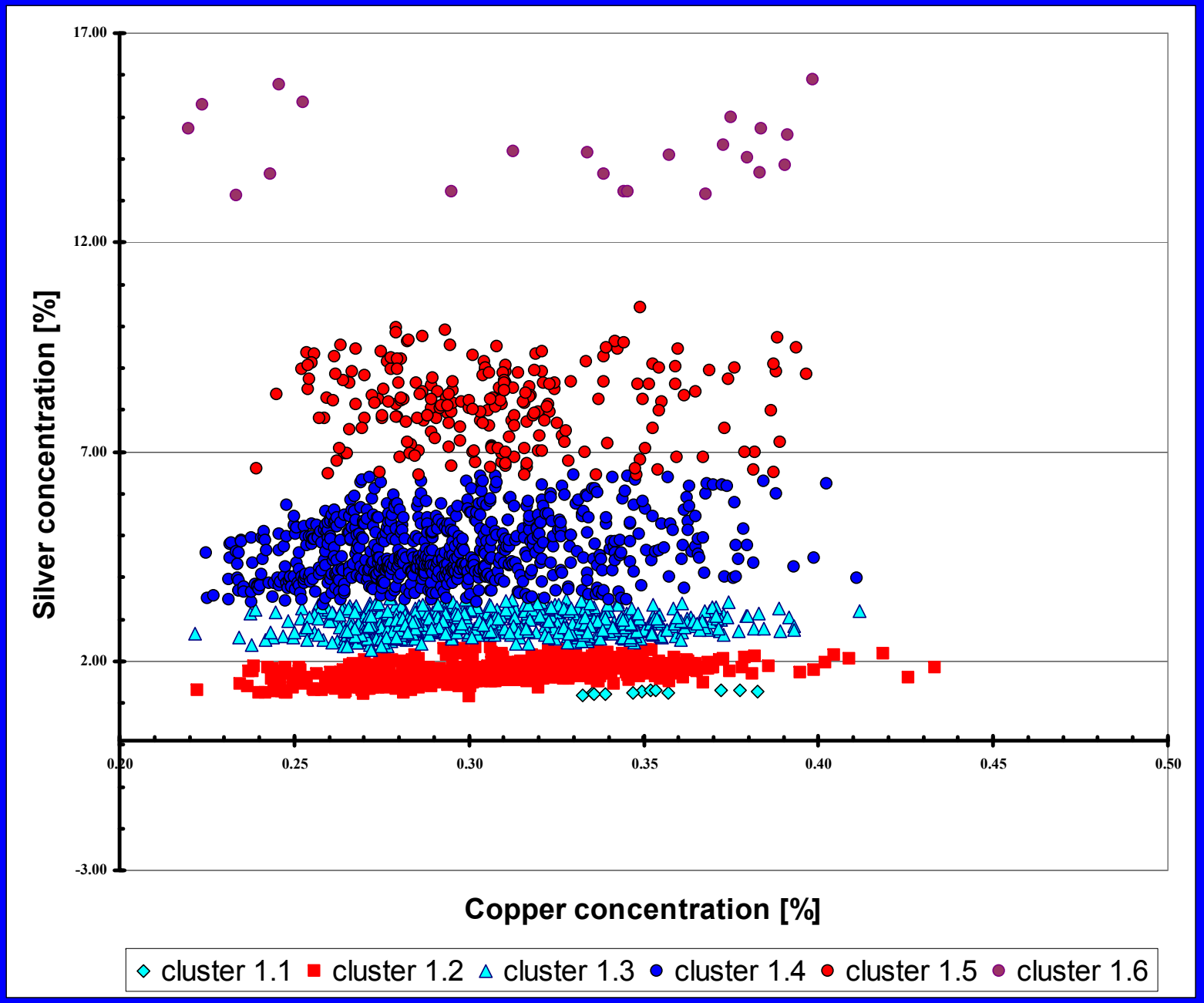
Hartmann, Studia Prehistorica, 1/2 (1978) 27



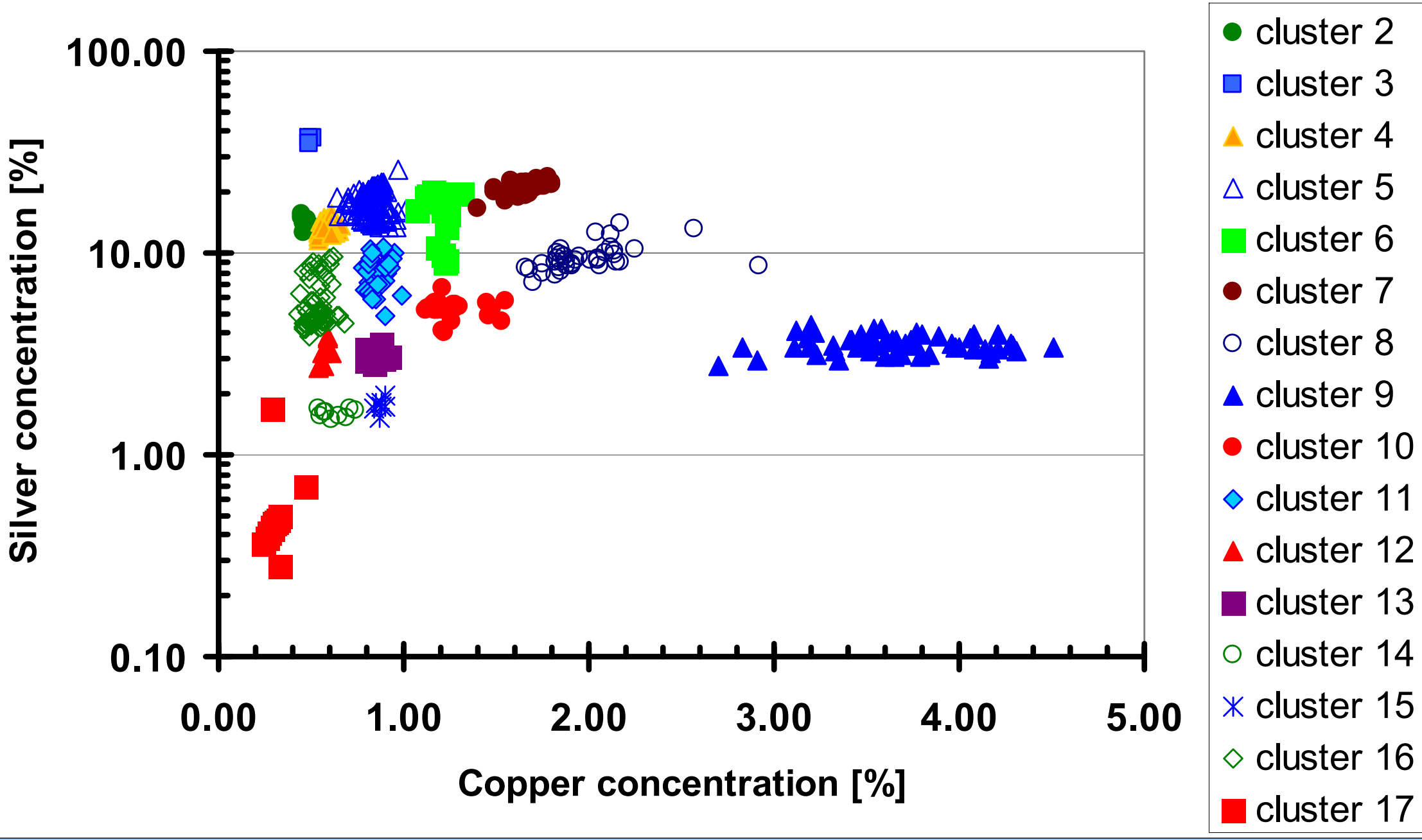
Distribution of the investigated gold objects according to the concentration of copper and gold



Distribution of the analyzed samples from Chalcolithic necropolis of Varna according to two dimensional diagram of copper *vs.* silver



Distribution of the gold samples from cluster 1 according to the concentration of copper *vs.* silver



Distribution of the clusters from number 2 to number 17 according to the concentration of copper and silver

The result of analysis shows that the gold used by the ancient people from Varna is natural gold, which has been gathered from different gold sources, practically alluvial gold.

Concentration

Gold: from 62.7 to 99.4%

Silver: from 0.4 to 36.8%

Copper: from 0.2 to 4.5%

All determined concentrations are in the range of natural concentration of silver and copper in gold

77 of the analyzed samples were produced using electrum (natural alloy of gold and silver with concentration of silver higher than 20%).

The mean concentration of silver in these samples is 22%.

The mean concentration of copper in these samples is 1.3%.

Three objects show very high concentration of copper

Copper: 33.88%; 34.95%; 36.22% **(35.02 ± 0.96)**

Silver: 14.1%; 13.9%; 14.1% **(13.9 ± 0.1)**

Gold: 52.02%; 49.98%; 51.15% **(51.05 ± 0.84)**

These three rings could be accepted as the oldest alloy produced by man!

Problems for the future (next year)

1. Analysis of the gold finds from Varna using LA-ICP-MS and ICP-MS

1.1. Calibration of the apparatus

1.2. Validation of the results

2. Analysis of geological gold samples using ICP-MS and LA-ICP-MS

3. Statistical evaluation of the analytical data

LA-ICP-MS: ready for work

The investigation of gold from necropolis of Varna was carried out through financial support by the National Science Fond of Bulgaria (contract ДО-02-60/10.12.2008)

Dr. Boyka Zlateva-Rangelova

Dr. Valentina Lyubomirova

Dr. Boyan Todorov

Prof. Dr. Rumyana Djingova, DSc

Dr. Kalin Dimitrov

Assoc. Prof. Dr. Vesselin Kovachev

Благодаря Ви за вниманието

THANK YOU

FOR YOUR ATTENTION

ICH DANKE IHNEN FÜR DIE AUFMERKSAMKEIT