Compositional classification of ceramics: Principles and examples

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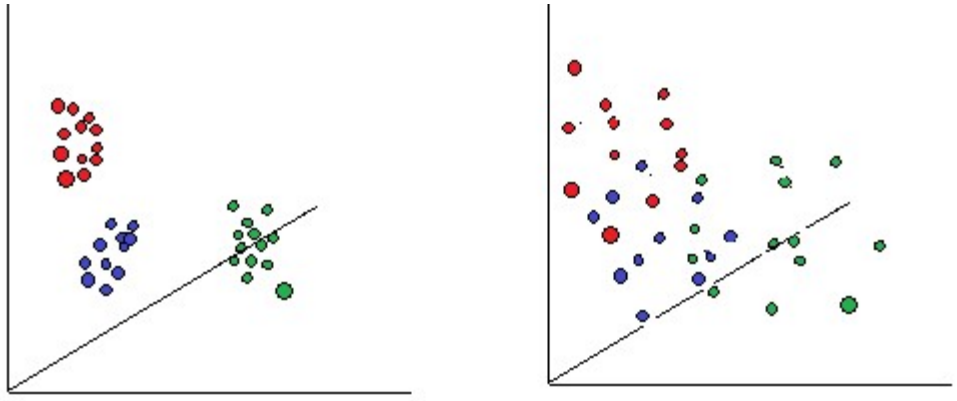
Outline:

- The rationale of compositional classification (fingerprinting)
- Premises and postulates
- Typical problems and capabilities of fingerprinting
- Sources and range of variability, Selection of useful elements
- Uncertainty of results and variability among classes
- Key aspects in research design: The need for inter-disciplinary approach
- Compositional classification: main steps
- Examples of application of compositional classification
- Concluding remarks and recommendations

The rationale

- There are similarities in composition within a given class of objects (compositional chemical units)
  - Objects have been produced using raw materials from a given source within some time period
  - During this period, no significant changes have occurred in manufacturing practice
  - The given class is associated to a meaningful context
    - In archaeology: timeframe / community / region / group
    - In art: Artist / master / technology or style
- The dissimilarities across different classes are of a larger extent than those found within each of the classes



The main premises

- There are similarities in composition within a given class of objects (compositional chemical units)
  - Objects have been produced using raw materials from a given source within some time period
  - During this period, no significant changes have occurred in manufacturing practice
  - The given class is associated to a meaningful context
    - In archaeology: timeframe / community / region / group
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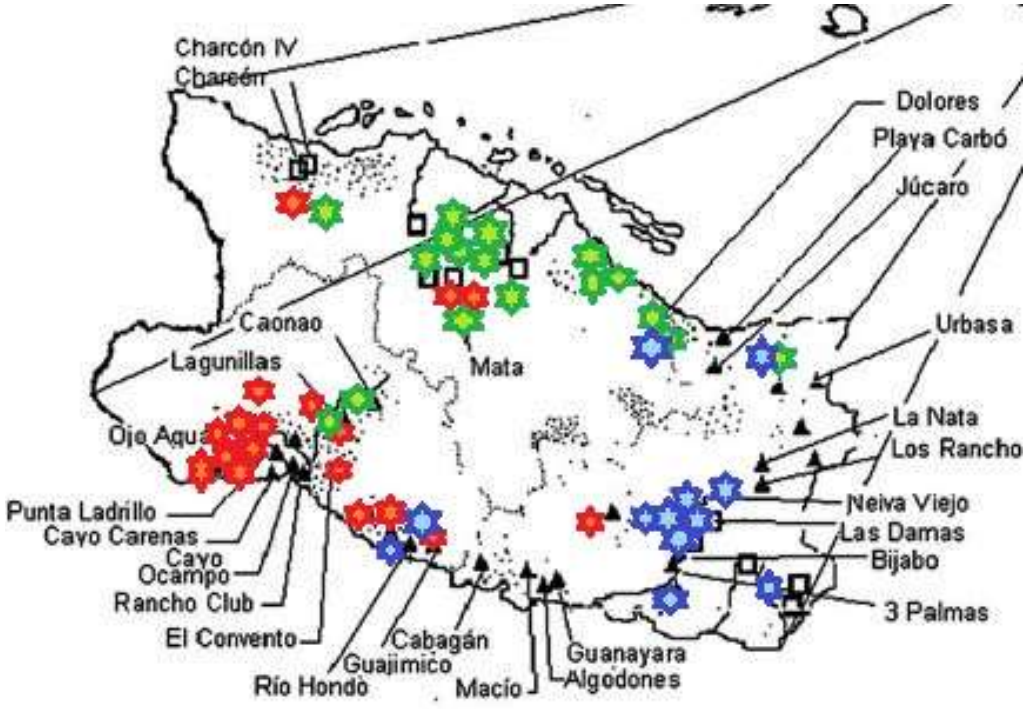
Postulates:

- Objects presumed to be produced at some loci are made using raw materials from sources around a reasonable distance
  - Distance is reasonable due to the assumed level of development (e.g. ancient communities ~ 7 km)
  - The use of ´foreign´ raw materials is well documented or logically sound

Postulates:

- It is common to find ´imported´ objects at a give site
  - The aureoles of distribution of objects must depict reasonable proportions and distances



Typical questions aided by fingerprinting

- Study of the ancient manufacture technology;
  - Identification of raw materials used
  - Understanding techniques of manufacture
  - Social interactions leading to changes in manufacture
  - Transculturation
- Provenance / authentication;
  - Identification of production loci
  - Establishing ancient trade routes
  - Authentication

Type of Analytical information

- Elemental analysis
  - X-ray Fluorescence analysis
  - Ion Beam Analysis (Particle Induced X-ray/gamma Emission, (PIXE / PIGE), Rutherford Back Scattering Spectroscopy (RBS)
  - Neutron Activation Analysis (NAA)
  - SEM-EDX
  - Laser Induced Breakdown Spectroscopy -LIBS
- Structural Information
  - Molecular analysis (Raman, FTIR)
  - Mineralogical/Crystalline phase analysis (TOF-ND, XRD)
  - X-ray Absorption Near Edge Structure (XANES)
  - Extended X-ray Absorption Fine Structure (EXAFS)

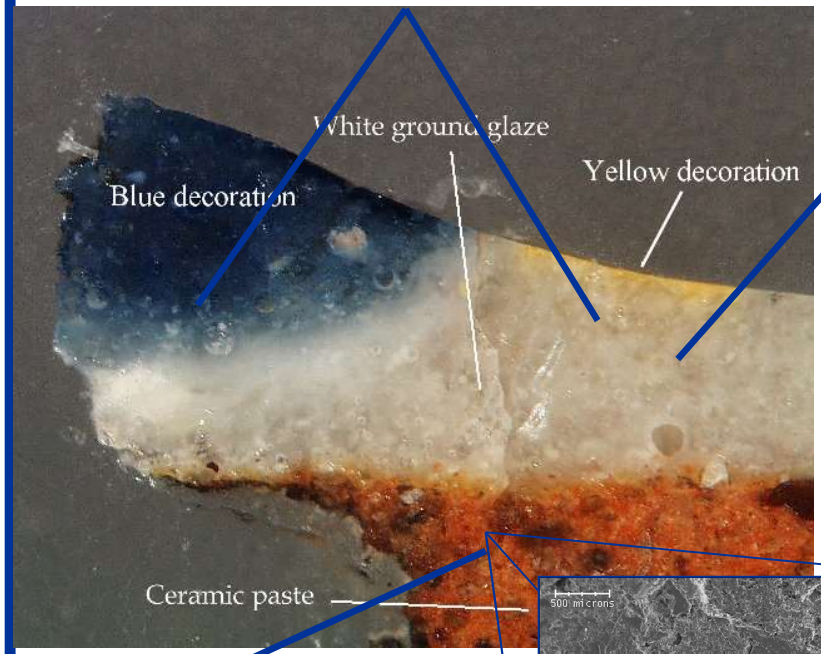
Each of the techniques provides certain information, but it is by far not enough for solving complex problems!

Useful combination in the case of ceramics

- Elemental analysis
  - Provides basis for multivariate statistical analysis
  - Useful to make inferences on procurement areas vis a vis the study of geological background
- Mineral identification
  - Serves to identify most likely areas of origin of raw materials
  - Presence of not fused mineral grains provides hint on temperature of firing
- Structural Information
  - Insights into technology of manufacture
- Dating
  - Time frame allocation, probably the more valuable information

Ceramics: What to llok for?

Color decorations…which can be quite heterogeneous



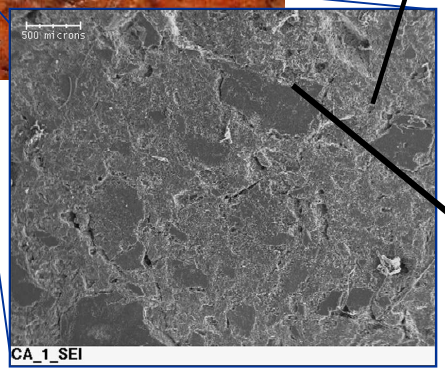
Ground glaze:

Proportions of major constituents (Alkali or lead oxides, tin oxide, aluminum from using clays, etc.)

Trace elements in the main constituent

Fired clay fraction:

Elements that have higher variability in the geological diversity, and which concentrate in hydrolyzed sediments



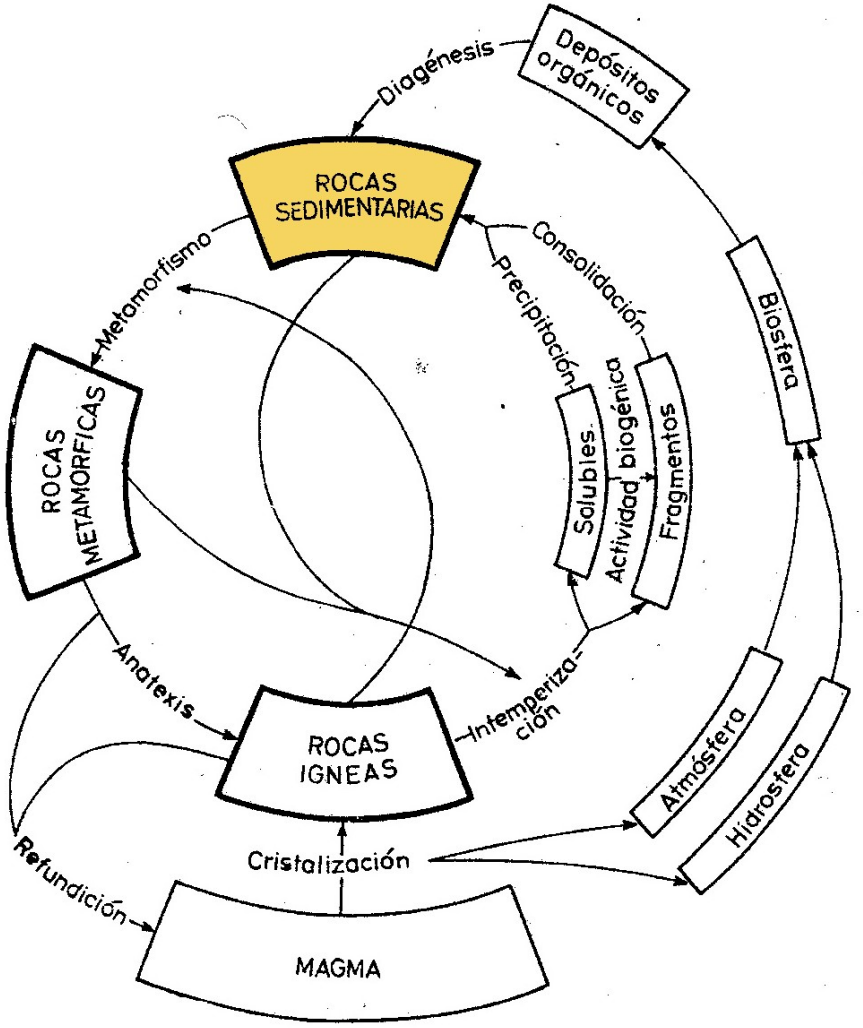
Ceramic fabric

Temper inclusions:

Elements that form the more abundant minerals

Sources of differences:

- Raw materials
  - Origin and intrinsic differences (geology, mineral sources)



Sources for differences:

- Raw materials
  - Origin and intrinsic differences (geology, mineral sources)
- Manufacture / technology recipe
  - Changes due to development / improvements
  - Modifications due to interactions / transculturation processes
  - Substitution due to *force majeure*
- Imported items
  - Trade / exchange
  - Migration routes

Useful elements for Fingerprinting

- Stone objects
  - Fe, Cr, Zr, Th (high variability in igneous rocks);
  - Y and REE (stages in crystallization of igneous rocks);
- Obsidian:
  - Fe, Mg, S, trace elements
- Metal objects:
  - Alloy composition recipe
  - Trace elements accompanying major metals in minerals
  - Surface degradation processes (S)

Useful elements for Fingerprinting

- Ceramics
  - Analysis of paste
    - Na, Mg, K, Ca, Rb, Sr (feldspars);
    - Fe, Cr, Zr, Th (high variability in igneous rocks);
    - Y and REE (stages in crystallization of igneous rocks);
    - Sc, Ti (accessory minerals)
  - Analysis of thick surface decorations
    - Present in fine clay (same as for paste analysis)
    - Associated to pigments (Fe, Cu, Cr, Pb, Sb, As, etc)
- Glass objects / glaze layers:
    - Na, Mg, K, Ca, Pb, Sn (elements used to reduce the melting point)
    - Associated to pigments (Fe, Cu, Cr, Pb, Sb, As, etc)

Ceramics: useful elements for paste

Clay fraction: Elements that have higher variability in the geological diversity, and which concentrate in hydrolyzed sediments

- REE – Different ratio of heavy to light (group-association, the most common in sediments) or selective association
- Cr, Fe, Th, Zr – Large differentiation during the formation of the rocks

Igneous rocks	Cr (μg/g)	Fe (%)	Th (μg/g)	Zr (μg/g)
Peridotite, dunite	3400	6,30	3,9	60
Gabro	340	8,84	9,97	140
Diorite	68	5,63		280
Granite	2	2,48	14,0	460

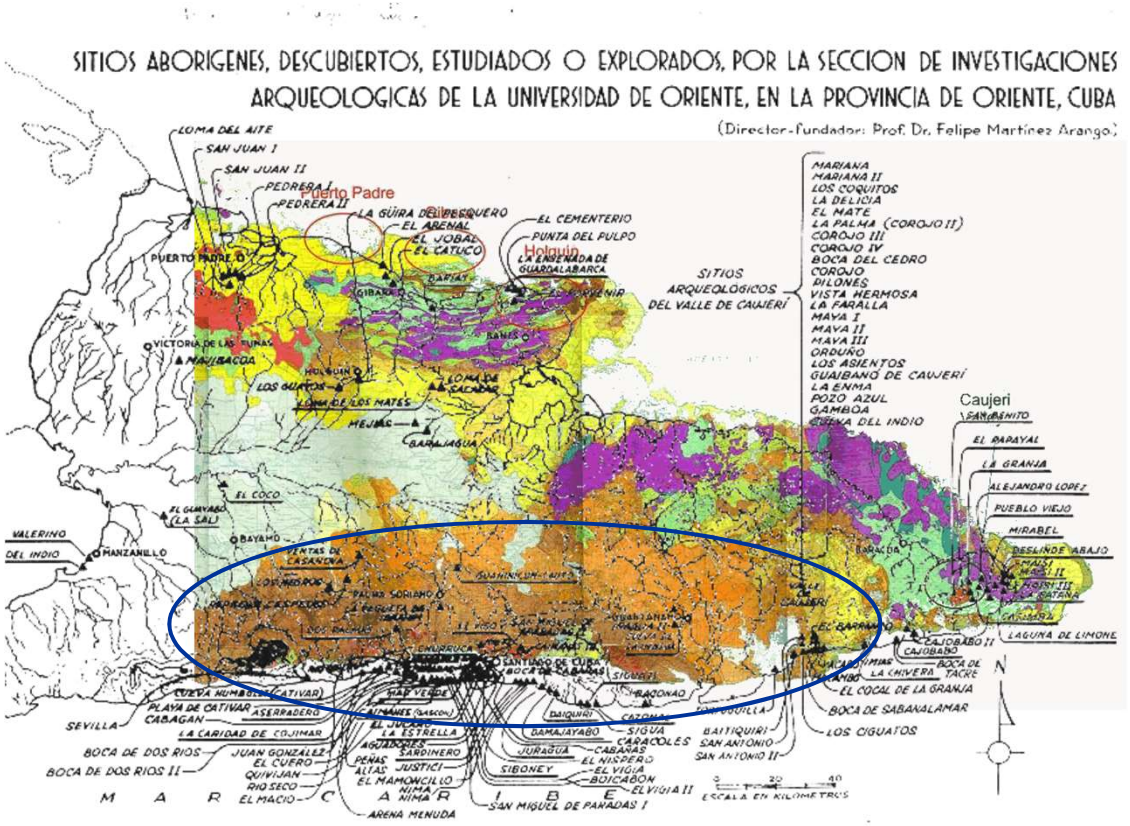
Temper inclusions: Elements that form the more abundant minerals

- Alkali and alkali-earth metals – Present in feldspars
- Other elements present in accessory minerals – Ti (rutile), Sc (ferro-magnesian), other in amphibole, pyroxene, mica

Research design
Example: Archaeological ceramics

Objective: to establish extent of trade and interactions along the densely populated southern coast

Intended method: elemental composition for fingerprinting



Limitation

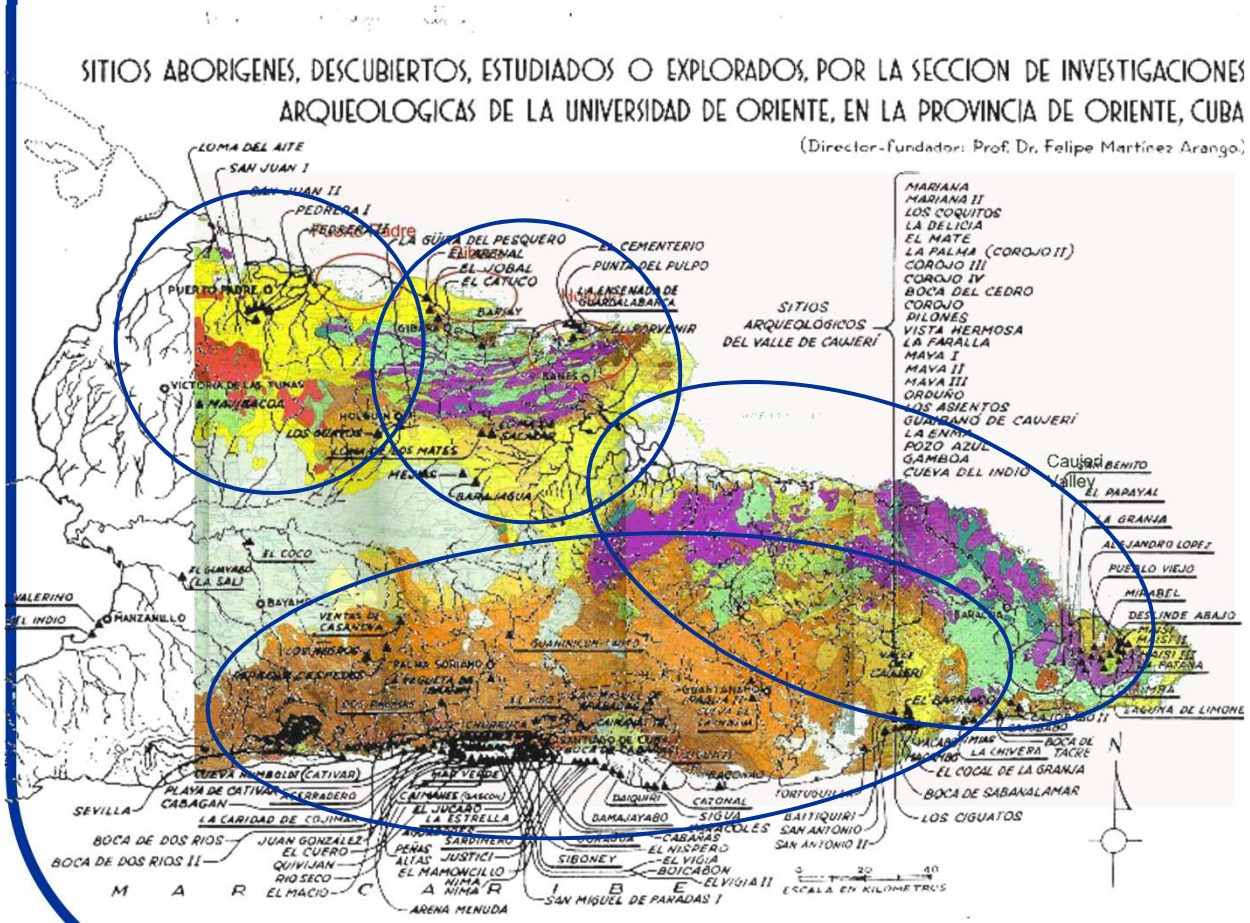
No geological diversity!

- No significant differences will be found in the composition of the samples

For 300 samples it would have implied
300 hours of measurement
40 hours of spectra processing and calculations
30 hours of unsuccessful interpretation

Possible reformulation of research:

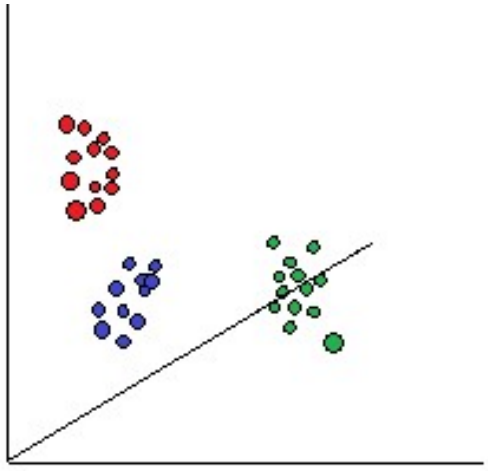
The possible results could only be

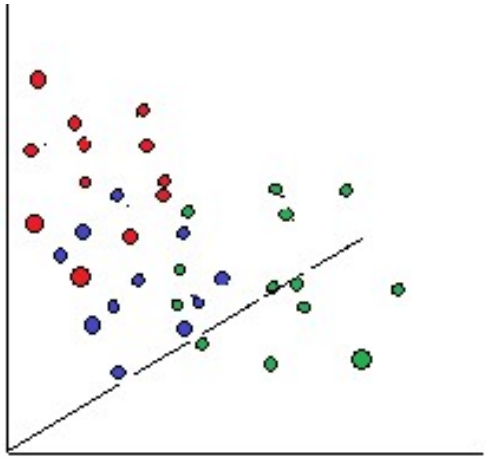


Studying sites across the whole region for finding intra-regional interactions

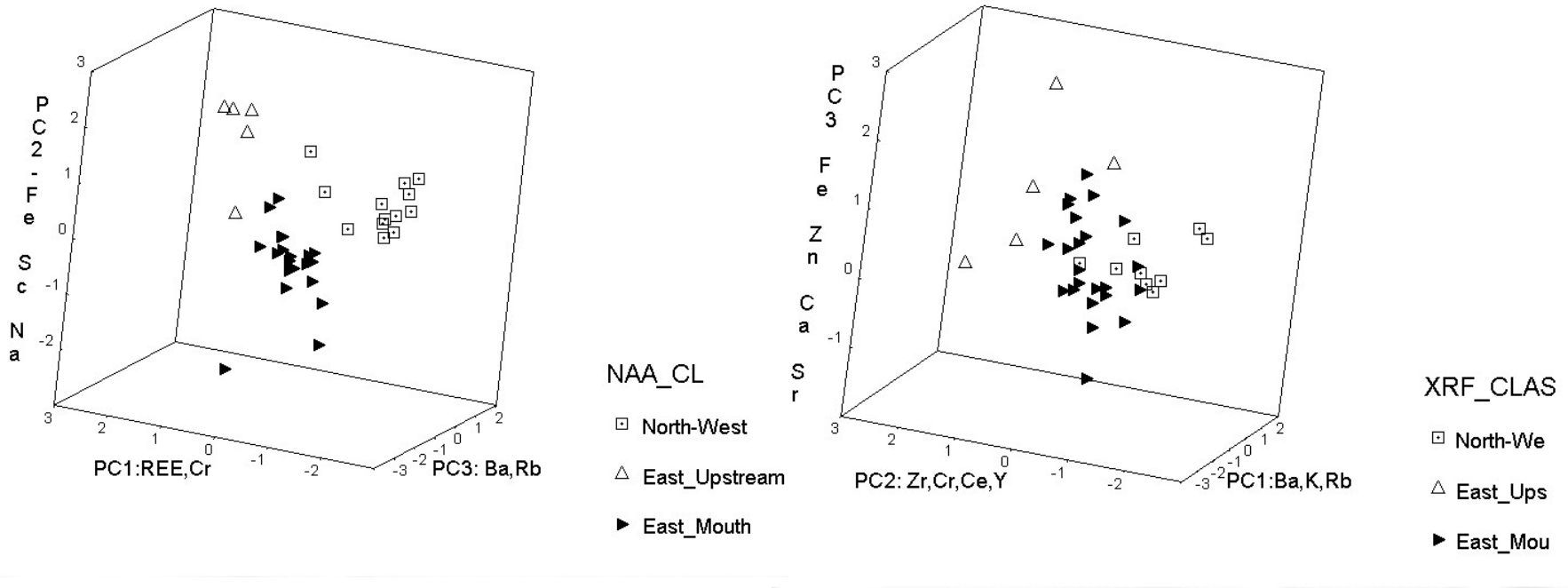
Additional requirements to data quality

- Variability of data
  - The uncertainty of results must be less than the variability among the groups





Influence of uncertainty on classification results



Padilla R. et- al., Analytica Chimica Acta, 558, Issues 1-2, 2006, 283-289

Additional requirements to data quality

- Representativeness
  - Suspected classes must be sufficiently and evenly represented

$$30 < N - 1 - \frac{(V-1)}{2},$$

preferably $60 < N - 1 - \frac{(V-1)}{2}$

- ● 17 samples
- ◇ 12
- ◘ 4
- \+ 3
- △ 1

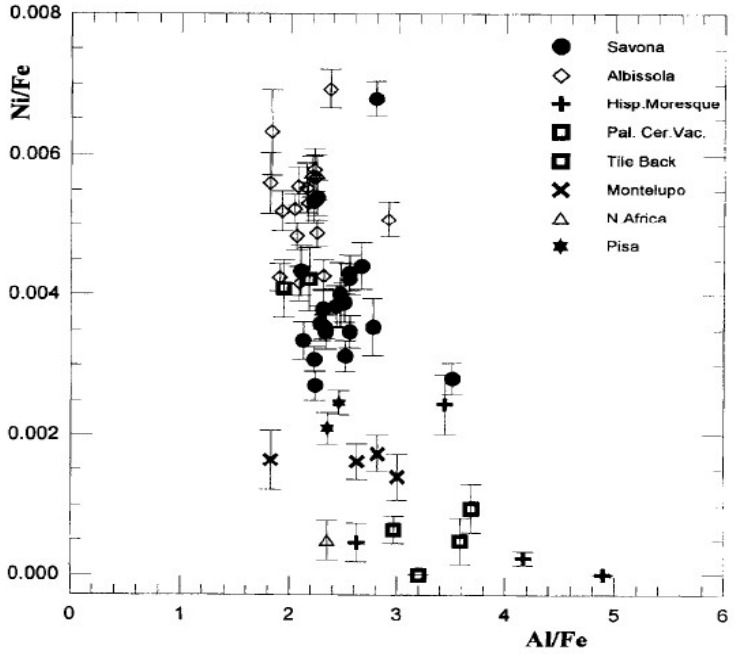
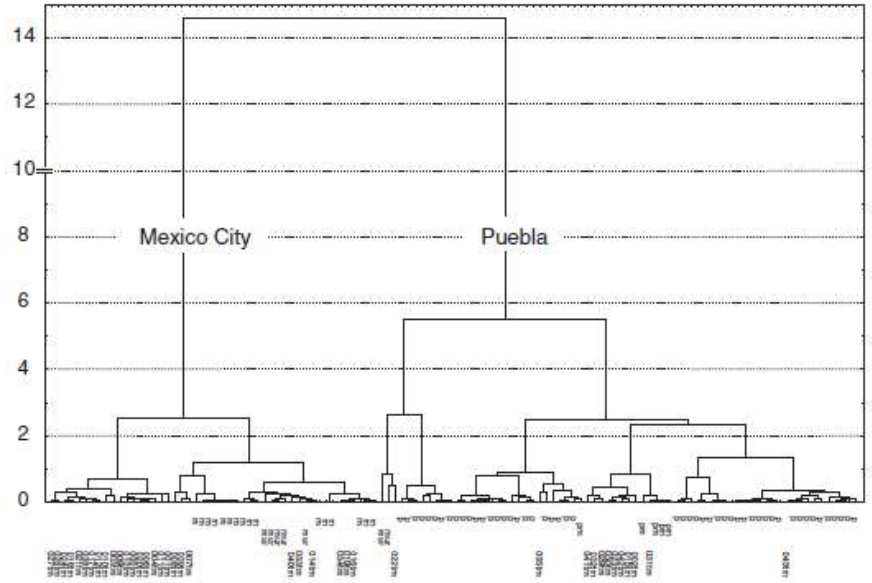


Fig. 4. The representation of all measured points in the (Ni/Fe)–(Al/Fe) plane.

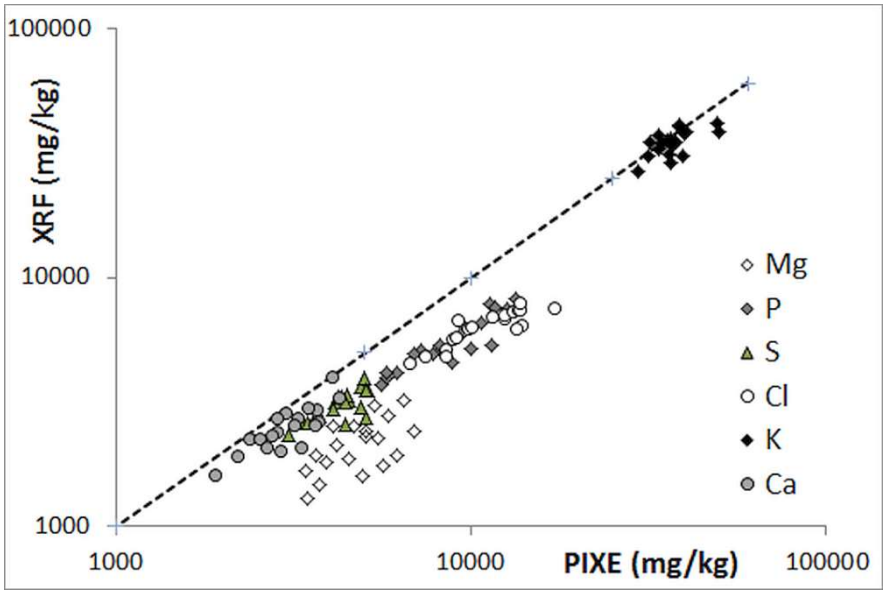
Additional requirements to data quality

- Statistical weighing
  - Results must be re-scaled or normalized as to avoid uneven weight in statistical interpretation
    - Log- procedure
    - Normalization procedures



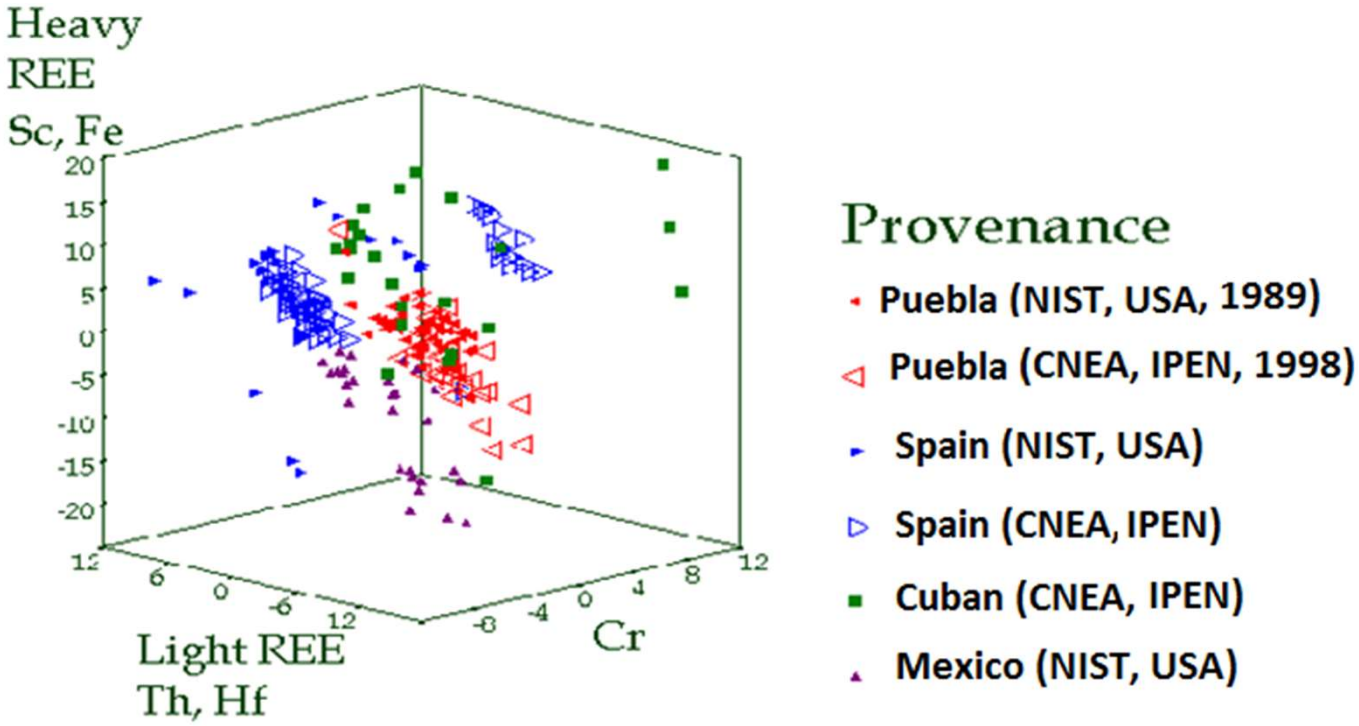
Additional requirements for fingerprinting

- Quality of results
  - Bias in results does not affect interpretation of results obtained by multiple techniques if ratios are of concern



Additional requirements for fingerprinting

- Quality of results
  - Comparison of results obtained by different techniques or laboratories is only possible if the sets of results are of comparable accuracy and uncertainty (validated methods under QC practice)



Data validation

- Outlier rejection
  - Outlying values must be revised to avoid occurrence of coarse errors.
  - Samples exhibiting outlying results to be re-analyzed
  - Up to 5 % of results may look “strange” in a dataset
  - Samples not matching to a compositional group might be due to import

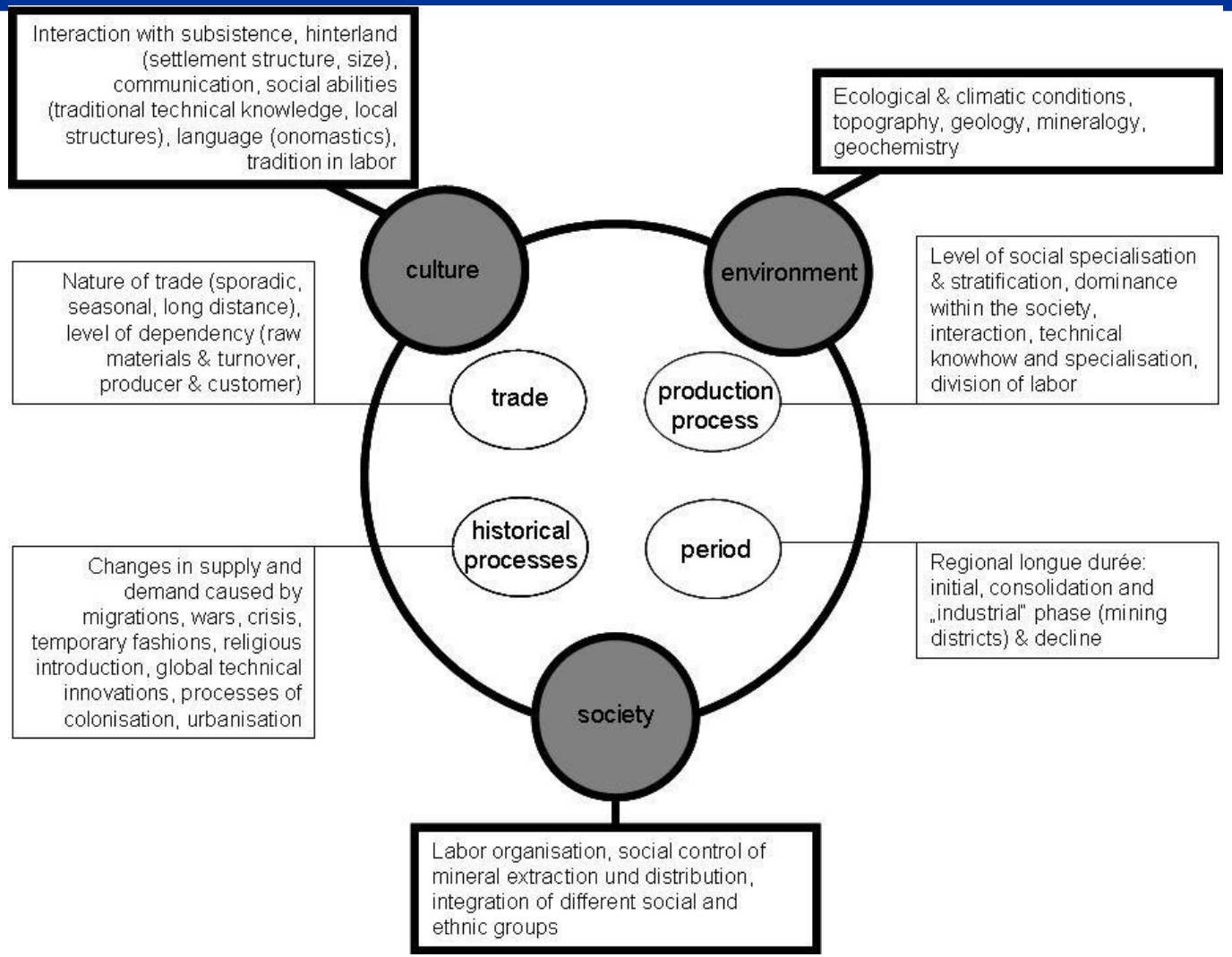
Key aspects in research design:

- Definition of questions
  - What is the problem?
    - Characterization information
    - Provenance / authorship
    - Technology practices
    - Interactions
  - Hypotheses formulated on the basis of the known contextual information
    - Initial hypothesis can be verified or,
    - Newly found evidence can lead to reformulating hypothesis

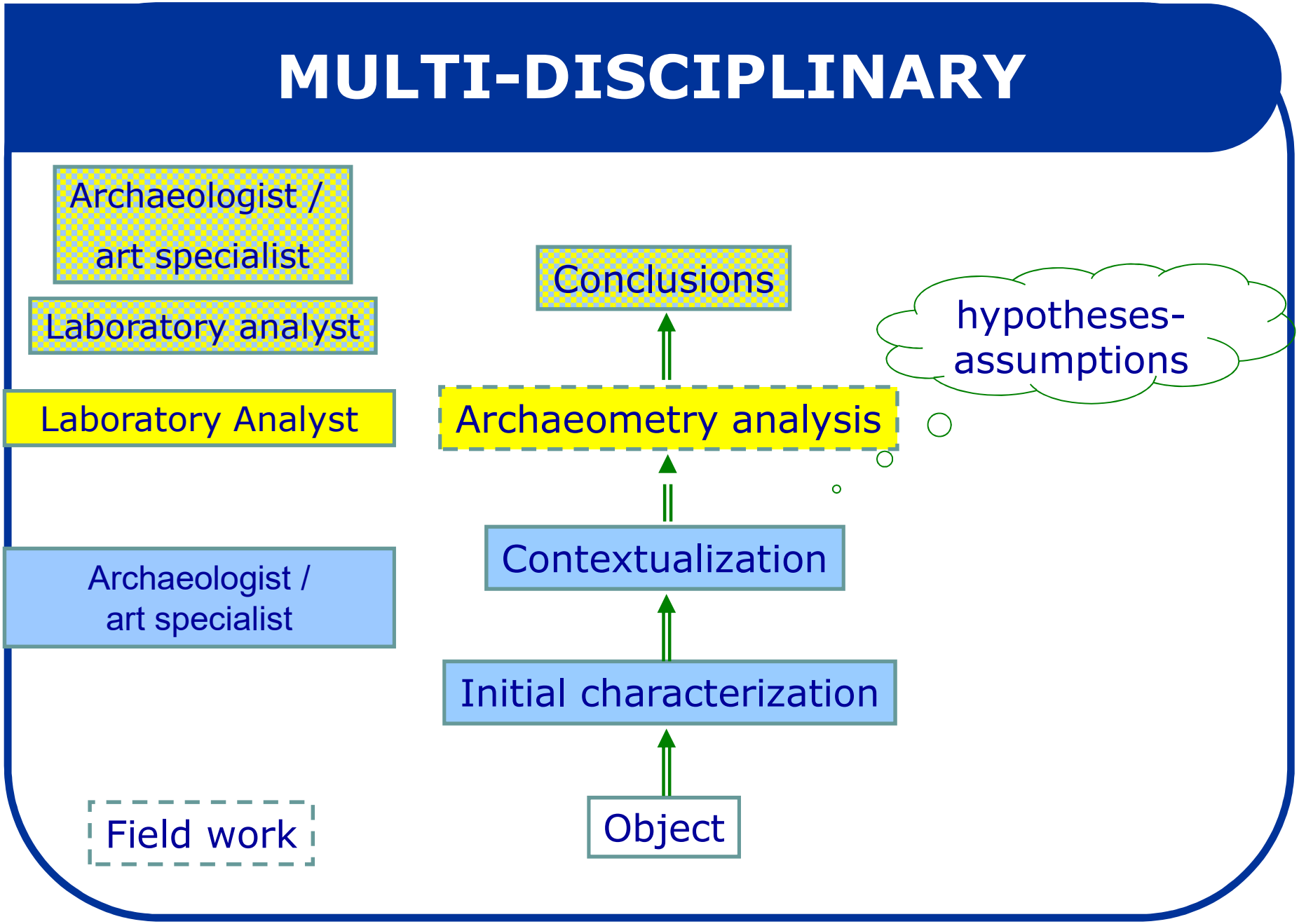
Key aspects in research design:

- Definition of questions
  - Strategies for
    - Sampling (random or problem oriented)
    - Types of analyses vs achievable information
    - Foreseen interpretation
  - Interpretation
    - Tools
    - Preliminary results
    - Re-sampling and complimentary analysis

The need for comprehensive contextualization



MULTI-DISCIPLINARY



Limited interpretation:

- Provenance study of Ligurian pottery by PIXE analysis
  (Published in 1996)

Na, Mg, Al,Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Zr, Ba, Pb.
Fifty samples, coming from archaeological excavations in the two towns of Savona and Albissola, as well as from Montelupo, Pisa, Spanish Moresque, North Africa…

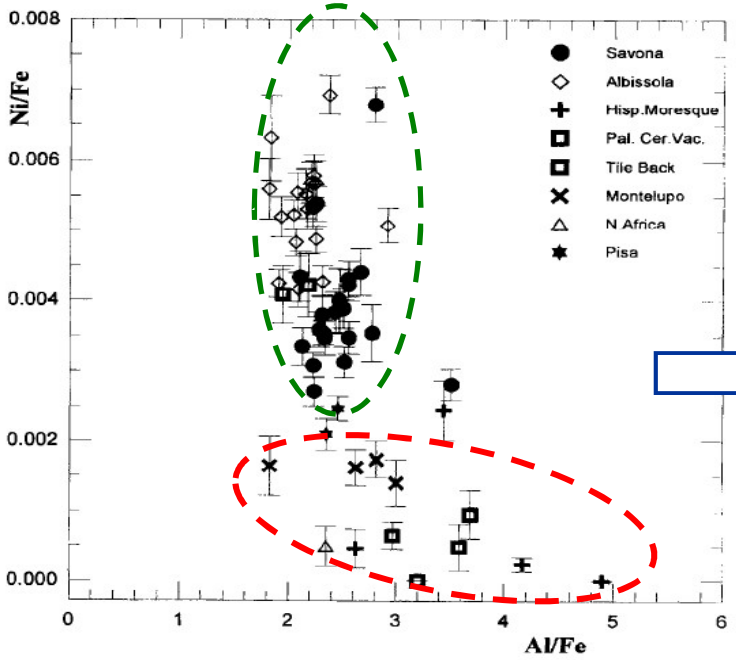


Fig. 4. The representation of all measured points in the (Ni/Fe)–(Al/Fe) plane.

Conclusions

- The PIXE analysis of potsherds has provided a mean of distinguishing, on the basis of major and minor elements, the pottery production of the two towns of Savona and Albissola, despite the proximity of the two centres.
- The statistical analysis of major and minor elements gives evidence of significant correlations amongst the subset of the S. Domenico findings and amongst the Hispano-Moresque samples and the tile from palazzo Cerisola Vaccioli in Savona, indicating also rather clearly that the Savona-Albissola production is all together well distinguished from the rest of the samples.

Limited interpretation:

- Provenance study of Ligurian pottery by PIXE analysis

- The pottery production of the two towns of Savona and Albissola, despite the proximity of the two centres.
  - Which criterion is used?
  - What are the reasons leading to such differences? Could be there other samples that wouldn't be different?
- Evidence of significant correlations amongst the subset of the S. Domenico findings and amongst the Hispano-Moresque samples and the tile from palazzo Cerisola Vaccioli in Savona
  - There are only three Hispano-Moresque! And only four of the Cerisola Vaccioli!
- Savona-Albissola production is all together well distinguished from the rest of the samples
  - Maybe also among them?

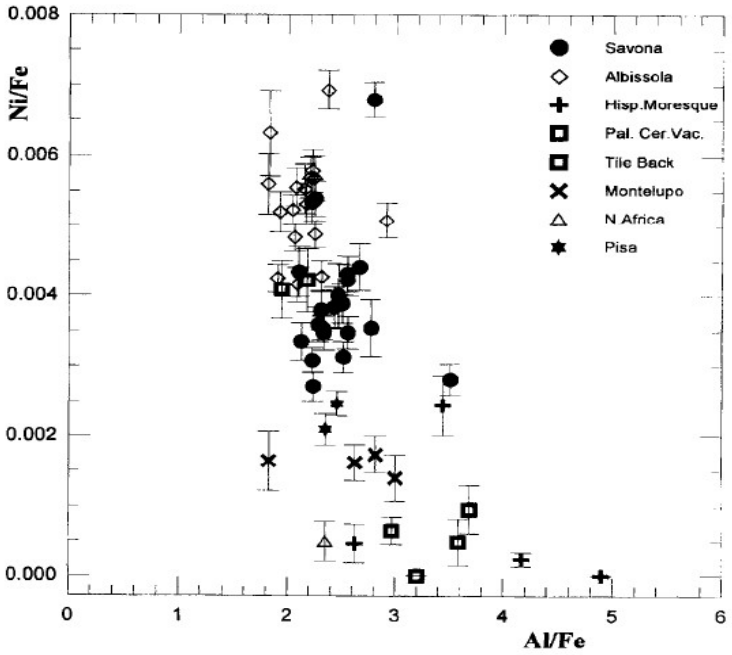


Fig. 4. The representation of all measured points in the (Ni/Fe)–(Al/Fe) plane.

INTER-DISCIPLINARY

Conclusions

Interpretation of results

Archaeometry analysis

Sampling design

Contextualization

Initial characterization

Finding

hypothesis-assumptions

Some references on interdisciplinary links

- Harbottle G., Chemical characterization in Archaeology, in ***Contexts for Prehistoric Exchange***; Earle T.K., Erickson J.E., Eds., Academic Press Inc., New York (1982) 13-51.
- A. J. Carpenter, G. M. Feinman, The Effects of Behaviour on Ceramic Composition: Implications for the Definition of Production Locations, *Journal of Archaeological Science* (1999) 26, 783–796
- H. Mommsen, Provenance determination of pottery by trace element analysis: Problems, solutions and applications, JRNC 247,3 (2001) 657–662
- M. S. Tite , A. J. Shortland, Production technology for copper and cobalt-blue vitreous materials from the New Kingdom site of Amarna – A reappraisal, Archaeometry 45, 2 (2003) 285 –312
- C.D. Lloyda, P.M. Atkinson, Archaeology and geostatistics, Journal of Archaeological Science 31 (2004) 151–165
- Ayelet Gilboa, Avshalom Karasik, Ilan Sharonc, Uzy Smilanskyb, Towards computerized typology and classification of ceramics, Journal of Archaeological Science 31 (2004) 681–694
- H. Mommsen, Short Note: Provenancing of pottery- The need for an integrated Approach?, Archaeometry 46,2 (2004) 267–271

Challenges to face in interdisciplinary research:

Subjective nature

- Fear to enter into unknown areas of knowledge
- Lack of knowledge / motivation
- Personal/Institutional vs. common interests
- Inability to establish strategic alliances
- Inability to recognize efforts fairly

Objective nature

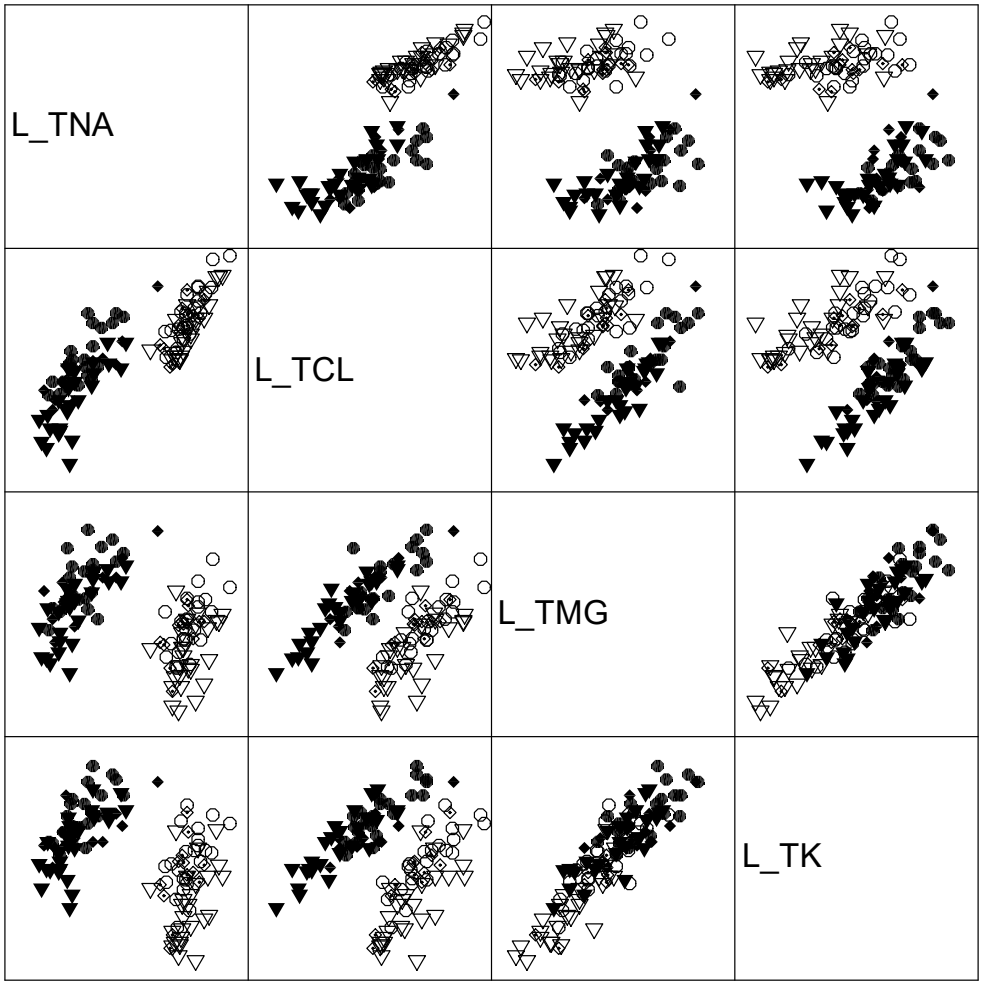
- Information asymmetries
- Insufficient financial means
- Lack of infrastructure (facilities, techniques, personnel)
- Not well established mechanisms for effective cooperation (at regional scale or even within the country!)

Main steps for fingerprinting

- Data pre-treatment
  - Rescaling or normalization procedures
  - Handling outlier results
- Statistical analysis
  - Data exploration in the search of some structure in variability
  - Reduction of dimensionality of data set (PCA)
- Iterative interpretation
  - Confirmation of data structure (re-definition of criteria for compositional groups)
  - Evaluation of group membership probabilities

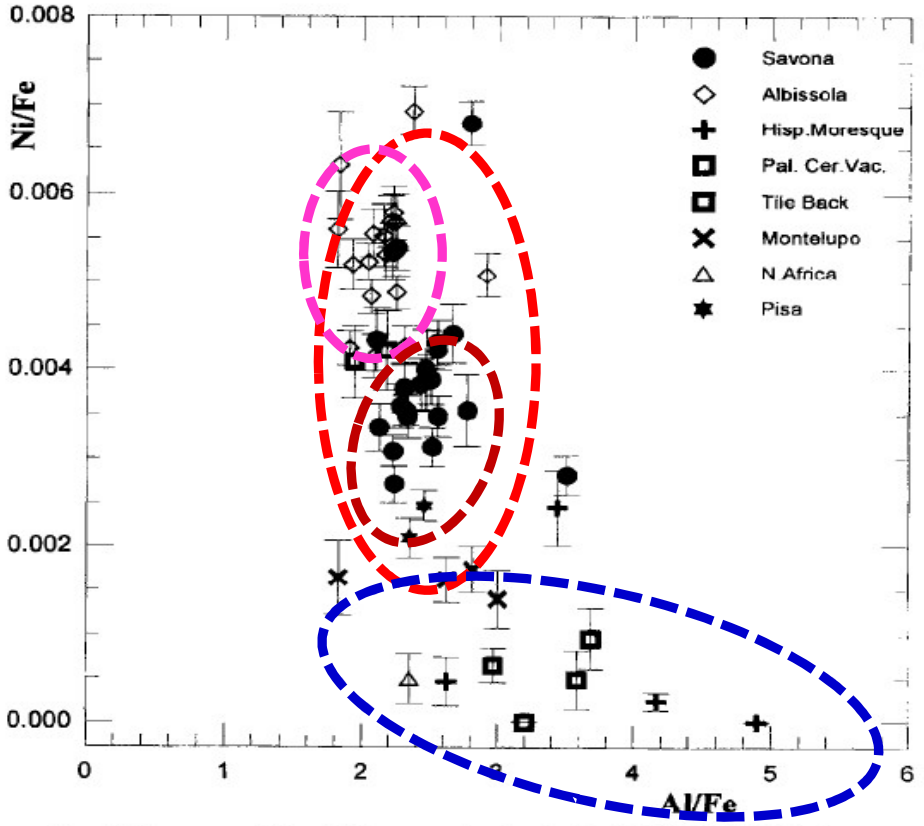
Data preliminary inspection

- Bivariate plots might indicate the elements contributing to variability in the data set
  - Samples need to be labelled by presumed classes.



Data preliminary inspection

- Bivariate plots might indicate the elements contributing to variability in the data set
  - Bivariate plots will reflect only the major difference, but some variability will not be easily noticed



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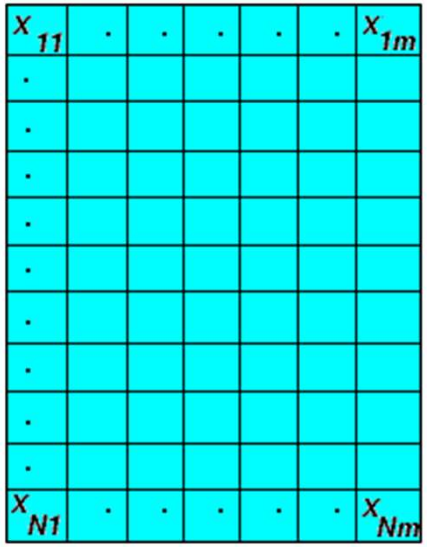
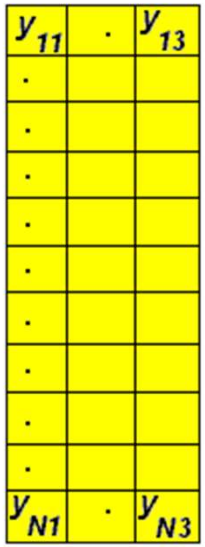
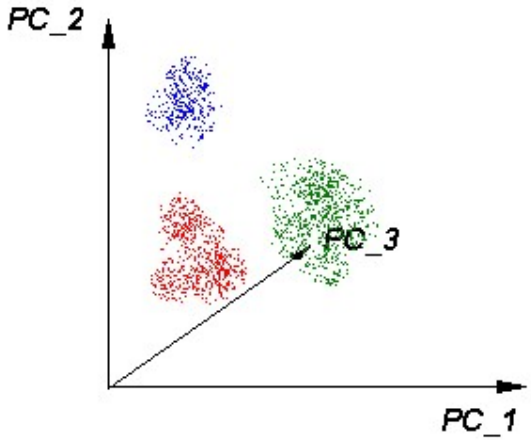
Principal Component Analysis



3.) PCA



4.) Ordination



1.) Scaling

2.) Elimination of outliers

Archaeological context
Historic records
Geography and geology
Stylistic description
SEM-EPMA

5.) Hypothesis validation or reformulation

6.) Canonical discriminant analysis
Group formation

PCA results

	Factor loadings						
	12 elements, 67 cases				10 elements, 142 cases		
	PC1	PC2	PC3	PC4	PC1	PC2	PC3
lg Ce	**0.901**	0.025	0.191	–0.036	**0.807**	0.187	0.233
lg La	**0.883**	0.080	0.349	0.045	**0.818**	0.222	0.385
lg Sm	**0.820**	0.016	–0.003	–0.050	**0.843**	0.191	0.152
lg Cr	**0.774**	–0.101	0.532	0.295	**0.756**	–0.066	**–0.634**
lg Yb	**0.760**	0.069	0.093	0.059	**0.732**	0.395	–0.031
lg Na	–0.286	**0.935**	0.130	–0.039	—	—	—
lg Fe	0.126	**0.845**	0.079	0.086	0.154	**0.916**	0.070
lg Sc	0.451	**0.673**	–0.075	0.180	0.342	**0.852**	–0.173
lg Th	0.146	–0.120	**0.745**	0.011	0.254	–0.047	**0.628**
lg Rb	0.137	0.078	**0.657**	0.171	0.038	0.074	0.402
lg Ba	–0.003	0.150	**0.521**	0.148	0.090	0.488	0.258
lg K	0.024	0.149	0.394	**0.894**	—	—	—

Example 1: Cuban aborigine ceramics

800 BP

1300 BP

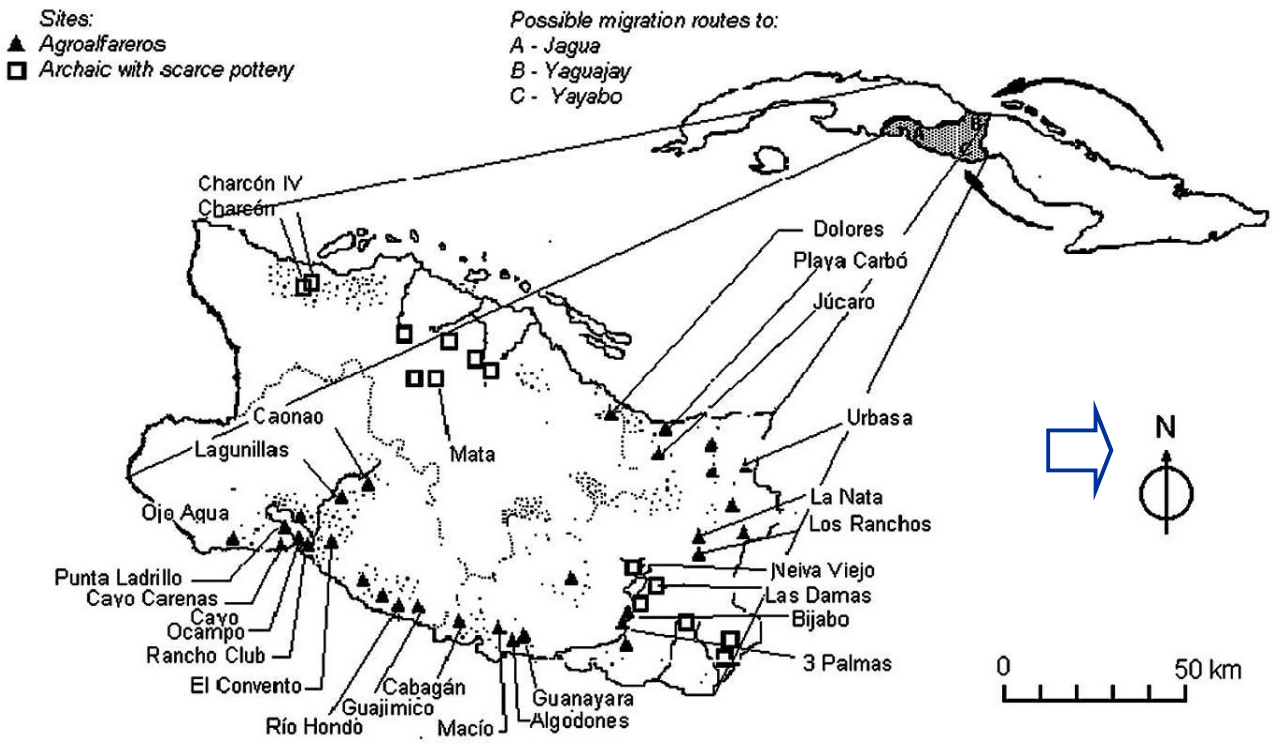
3000 BP

Taíno : Agriculture & pottery

Subtaíno Agriculture & pottery

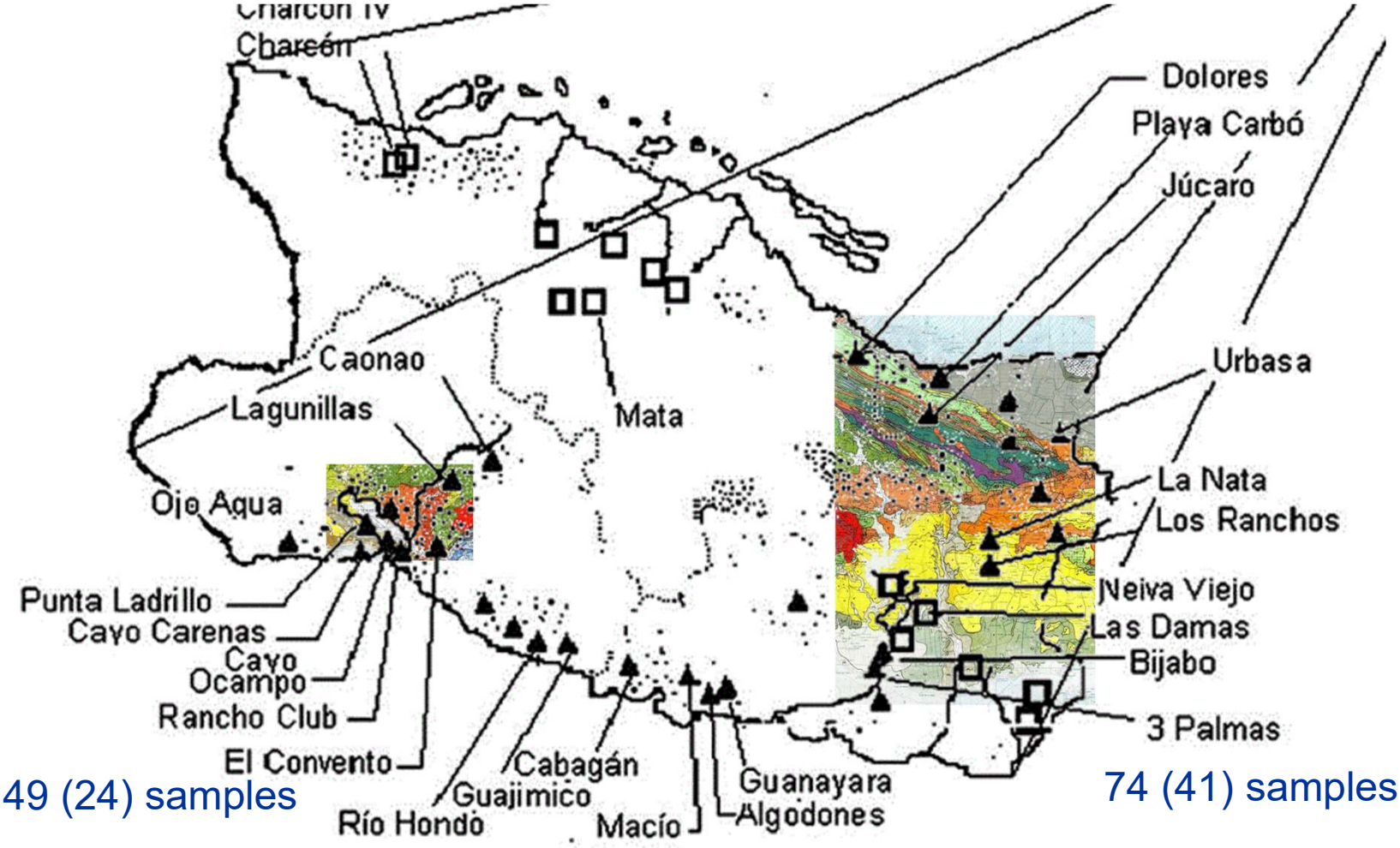
Archaic

PCA classification of Cuban aborigine ceramics (XIII – XV), Central region



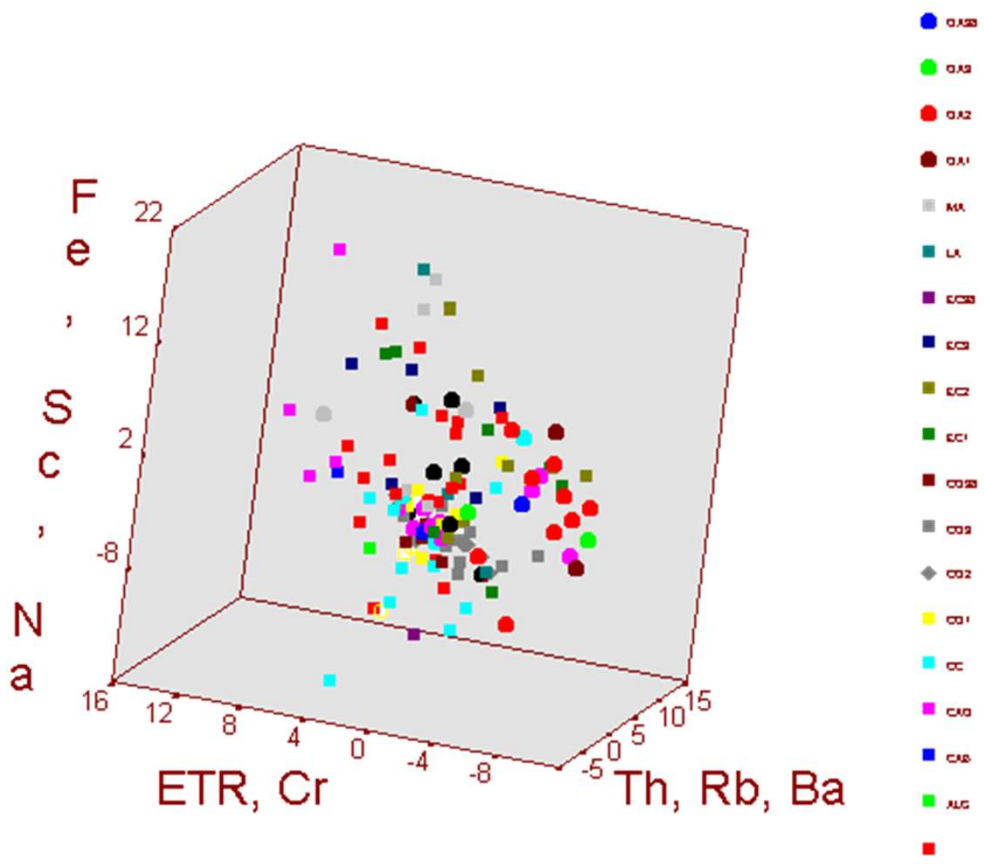
- 23 elements analyzed by NAA in 240 samples
- PCA analysis of results (data exploration)
- SEM-EDS analysis of samples

Example 1: Central region geological diversity



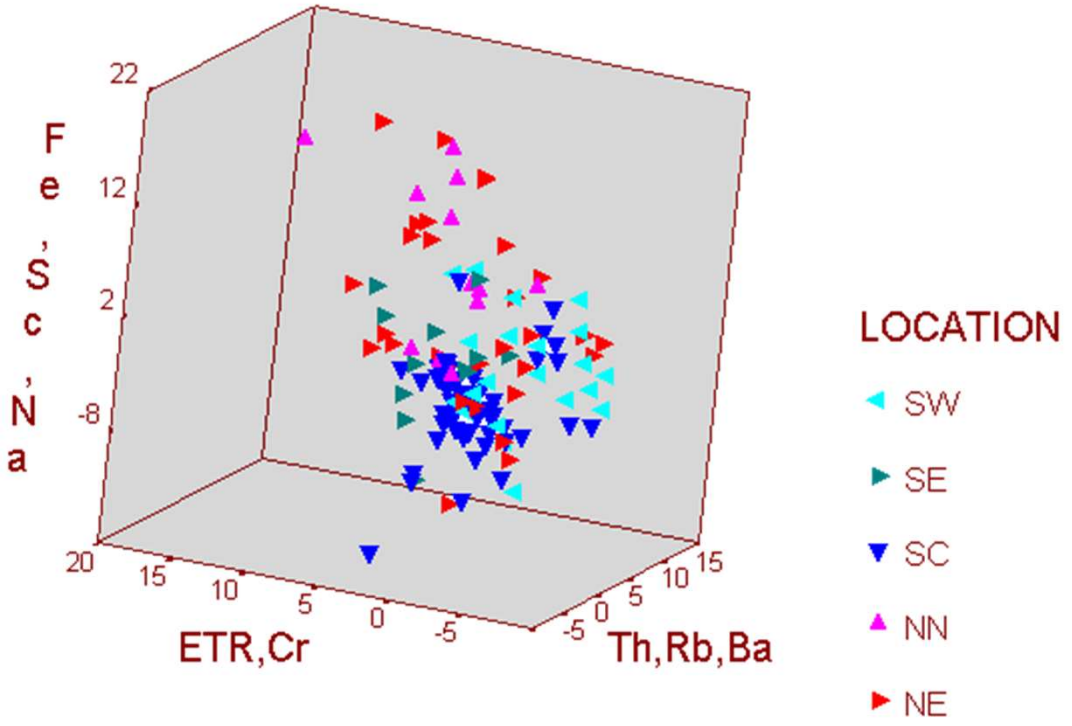
Classification based on PCA: defining classes

1.- By sites ?

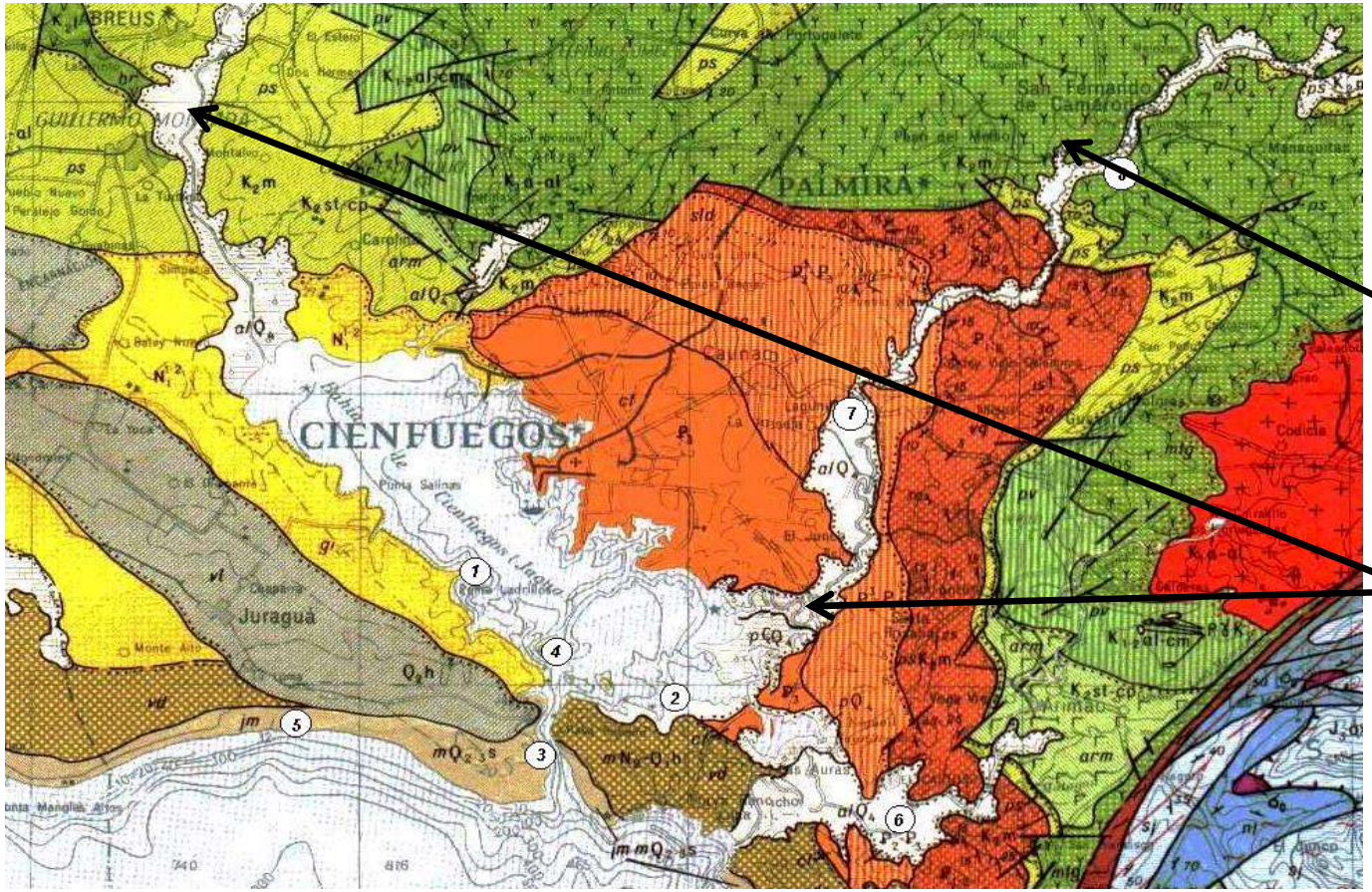


Classification based on PCA: defining classes

2.- By territorial location ?



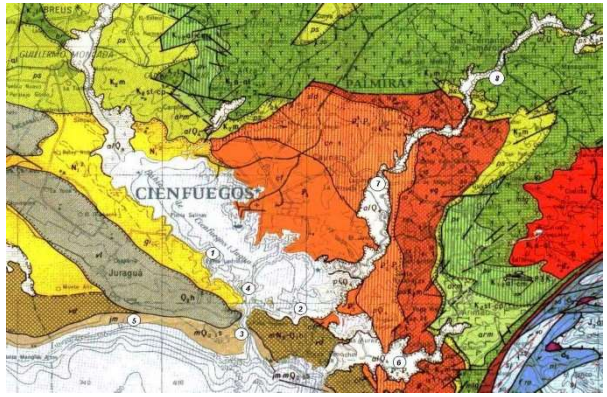
The geological diversity in Jagua region

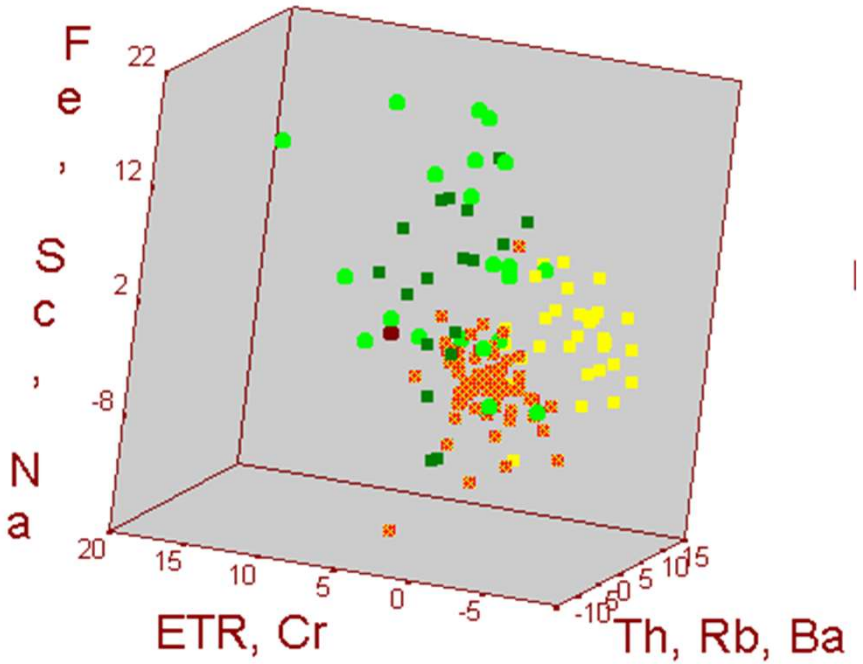


Study of the Geology and formations from which clays could originate

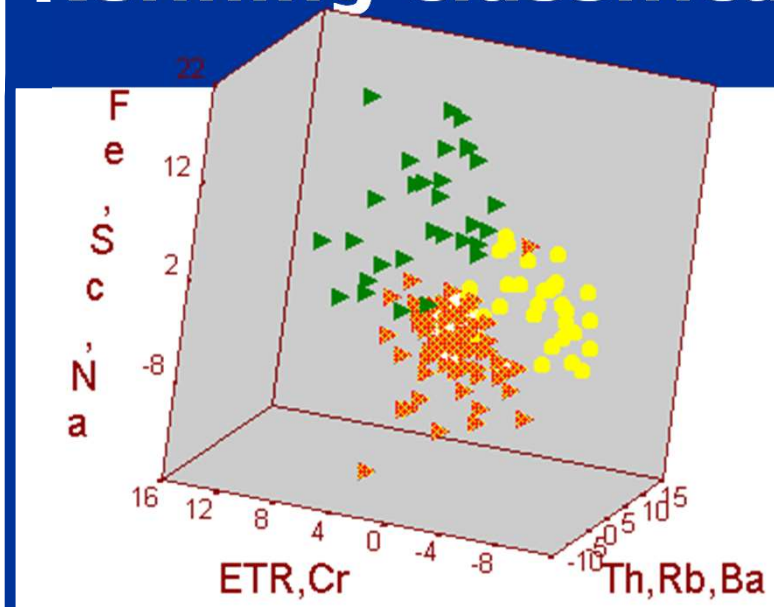
Classification based on PCA

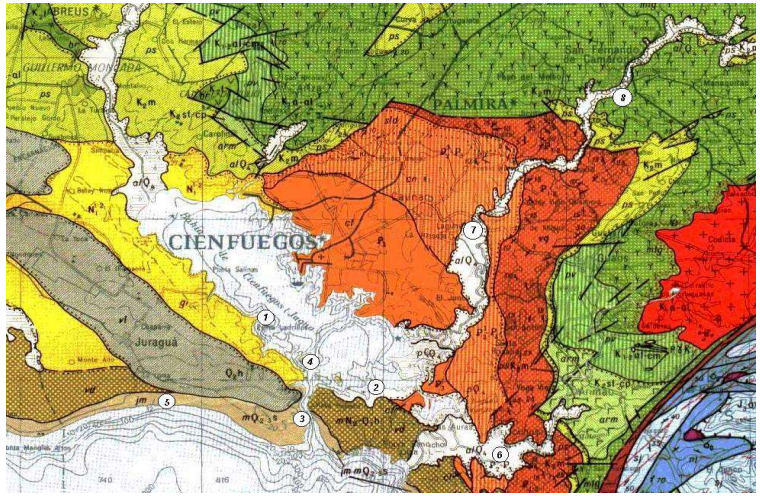
3.- By differences in composition
⇒ procurement materials





Refining classification groups





▲ Highest Th, Lower Cr, REE, Sc, Fe, Na.
Minerals: PLGC > QRZ > K-FLD

- Andesite-basalt
- Limestone, vitro-clastic tobaceous rocks

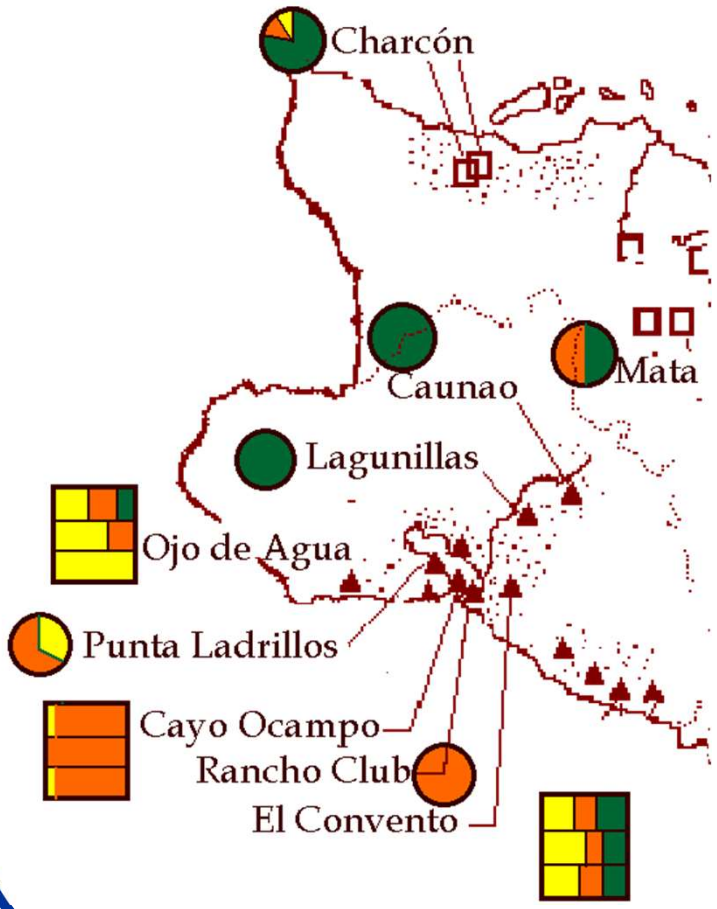
▲ Higher Cr, REE, high Sc, Fe, Na.
Minerals: PLGC > K-FLD > QRZ > BIOT > EPID > CLPRX
Large grain size → less erosion and weathering

- lava, basalt, landsite-basalt, andesite-basalt and breach

▲ Lower Cr, REE, Sc, Fe, Na.
Minerals: QRZ >> K-FLD >BIOT
Smaller grain size → more weathering of clays

- sand impurities in clays

Results from interpretation of classification



Inferences:

- The settlements around the bay had a well-consolidated manufacture
- El Convento resembles to have been a centre of intense exchange
- Ojo de Agua: change in the procurement zones during time
- Caunao and Lagunillas: Assimilation of potery manufacture skills

Ceramics from Colonial period: The context

Havana was an important hub for the Spanish fleets in their travels between the Metropole and the colonies

Ships loaded with treasures gathered in Havana waiting for the Armada to escort them in the trip to Seville

Rich collections of archaeological objects are found during the restoration works in old town

Example 2: The Majolica

Majolica(*): Ceramics originating in Spain from Moresque influence, well shaped from fine paste and decorated with tin-lead opaque translucid white glaze

(PbO ==> fusing agent)

(SnO2 ==> opacity)

Similar tchnologies: French Faience, Dutch Delftware

Columbia Simple

Catalana Azul/blanco

Yayal Azul/blanco

Sevilla Azul/Azul

Poublet

Puebla: Azul/blanco Polícromo

(*)Goggin, John M.: Spanish Majolica in the New World: Types of the sixteenth to eighteen centuries. Yale University, New Haven, 1968.

Classification problems:

- New typologies (not previously described) are found in colonial sites
    - What is their origin?

Santovenia[3]

Azul sobre blanco

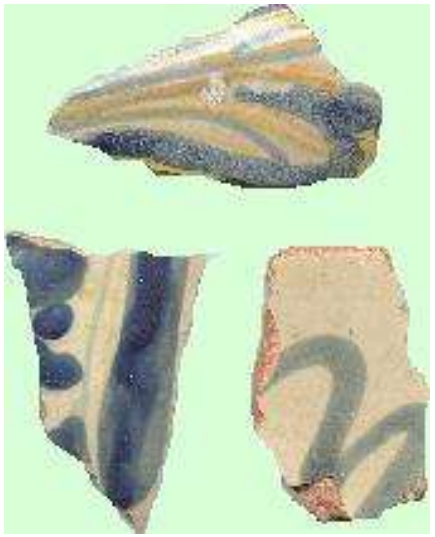
Polícromo

Spanish origin?

Classification problems:

- Some typologies resemble another well described styles, but the different appearance of the ceramic fabric leads to doubt

Spain



Mexico City

Puebla

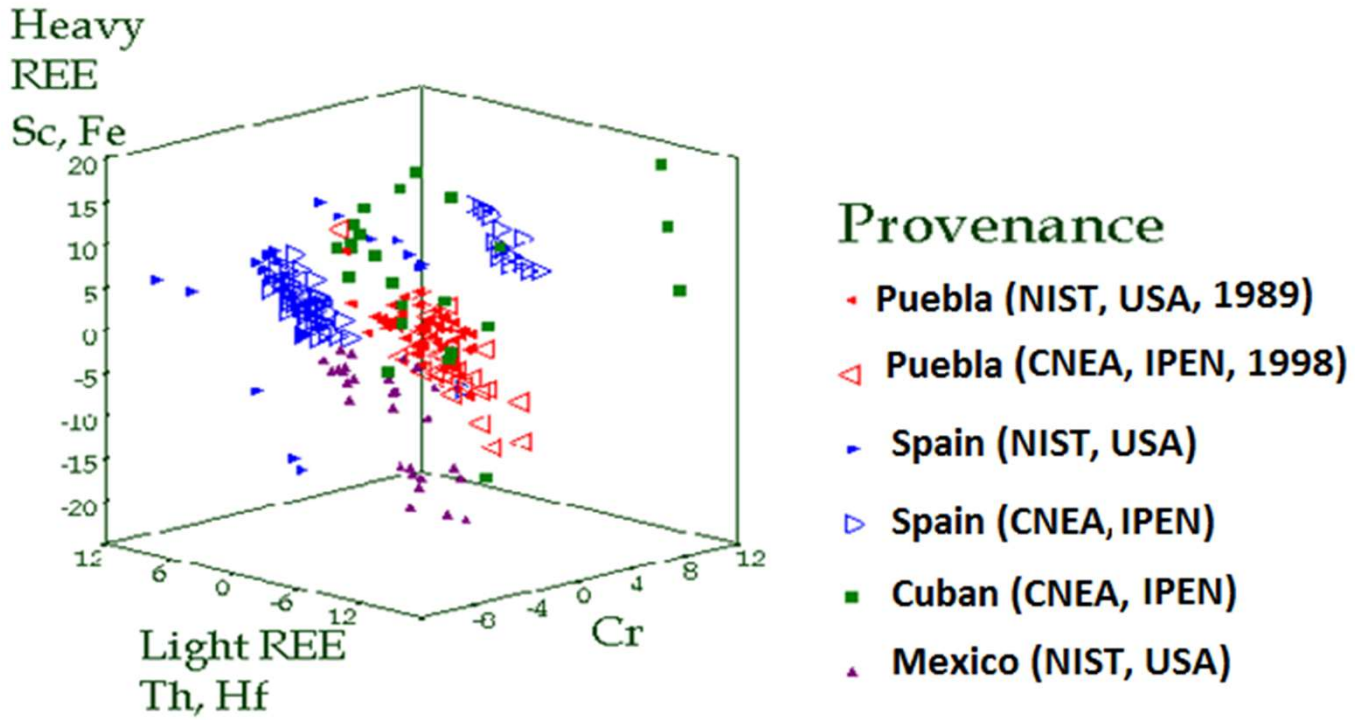
Spain?

Historical question:

- The presence of utilitarian ceramics, seemingly produced by local aborigines, in colonial sites raises as question whether their ceramic production (XVi – XVIII centuries) was used by Spaniards as a cheap choice

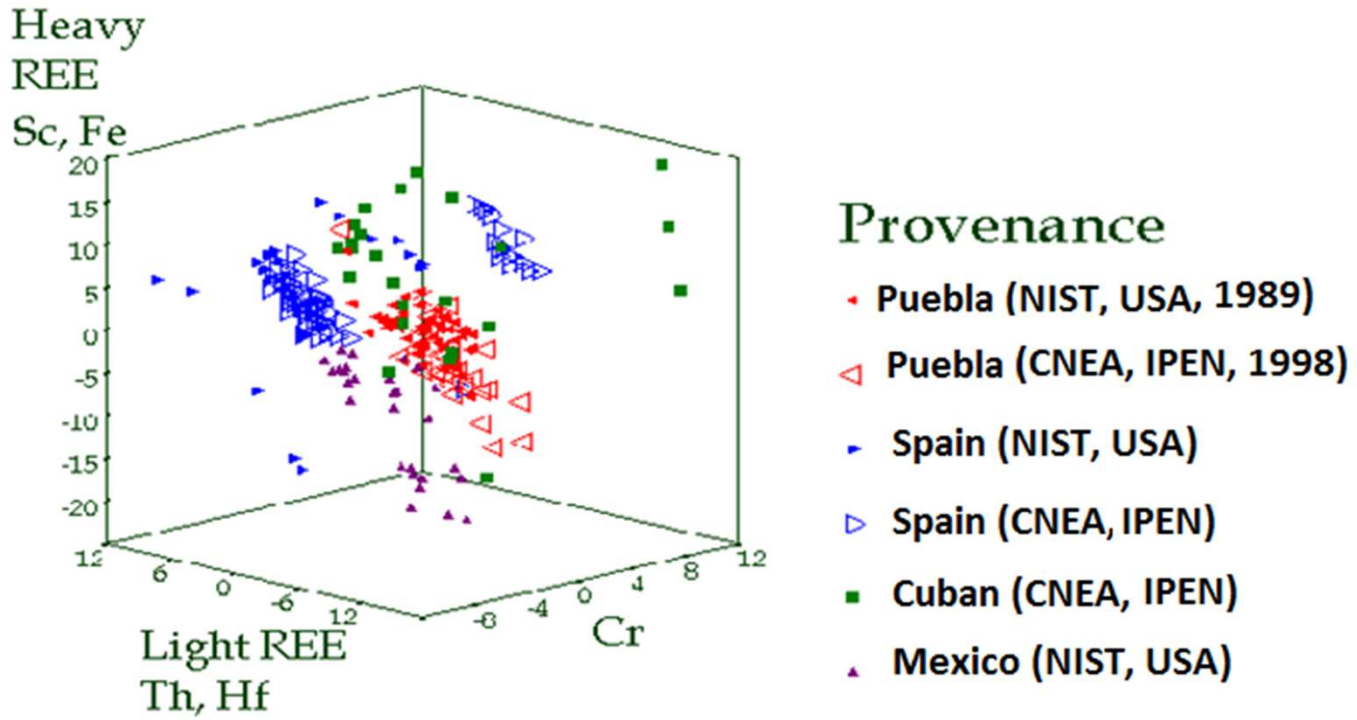
Results from classification based on paste composition:

The provenance of 80 % of samples, presumed from style, was corroborated



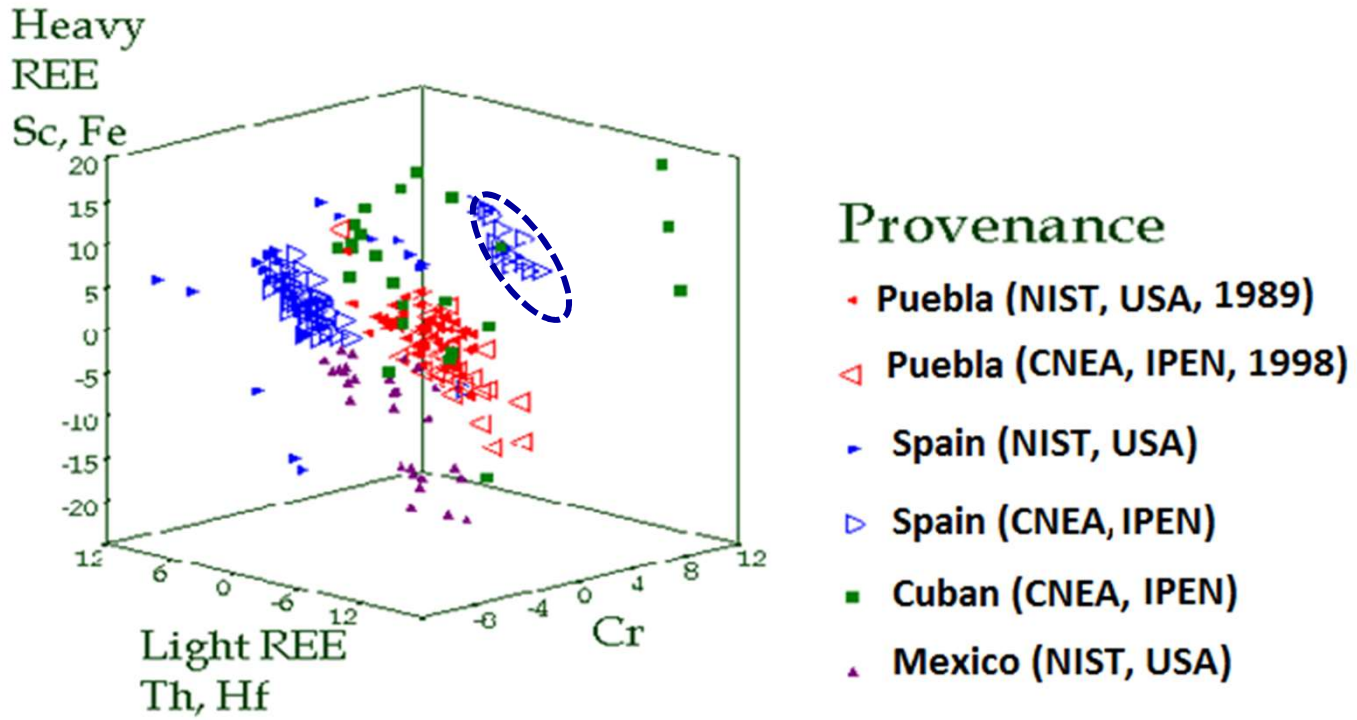
Results from classification based on paste composition:

Utilitarian ceramics did not match by composition to neither Spanish nor Mexican origin



Results from classification based on paste composition:

- A number of presumed *Sevilla blue on blue* ceramics did not match by composition to the presumed Spanish origin



The Blue on Blue problem:

- The stylistic features of Sevilla Blue on Blue are very similar to Italian Liguria
  ☹Samples can not be classified by appearance!

XRF analysis of the glazes

	Main compound	Other elements
SV - Polícromo	Red earth pigments (Fe)	Cr, Mn, Co, Ni
Abó - Polícromo	+ Naples Yellow ($Pb(SbO_3)_2/Pb_3(SbO_4)_2$)	Ca, Cr, Co, Ni, Cu, Zn

Yellow

	Main compound	Other elements
SV - Polícromo	Naples Yellow ($Pb(SbO_3)_2/Pb_3(SbO_4)_2$)	Ca, Cr, Zn
Abó - Polícromo		Cr, Ni, Cu, Zn

Green

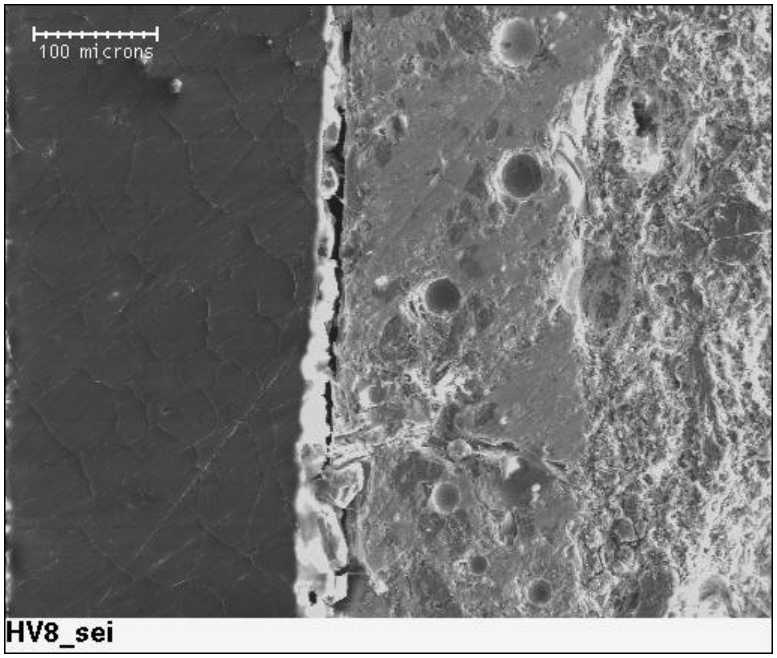
	Main compound	Other elements
Abó - Polícromo	Copper oxides	K, Ca, Cr, Fe, Zn
San Luis - Polícromo		K, Ca, Cr, Fe, Zn

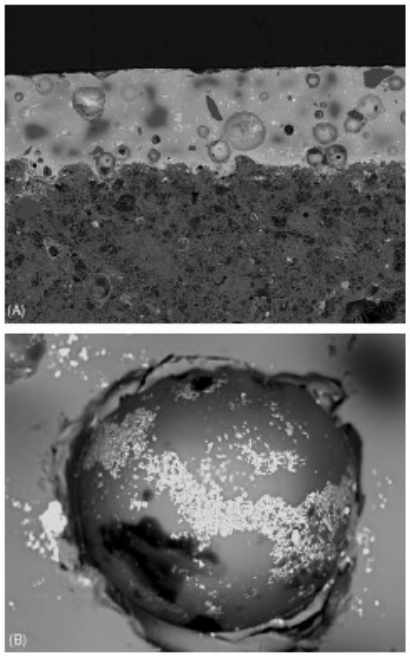
Black

	Main compound	Other elements
Abó - Polícromo	Iron / cobalt oxides	Ti, Mn, Ni, Cu, Zn
San Luis - Polícromo		Ca, Ni, Cu, Zn
Puebla – Polícromo		Ca, Ti, Mn, Ni, Cu, Zn

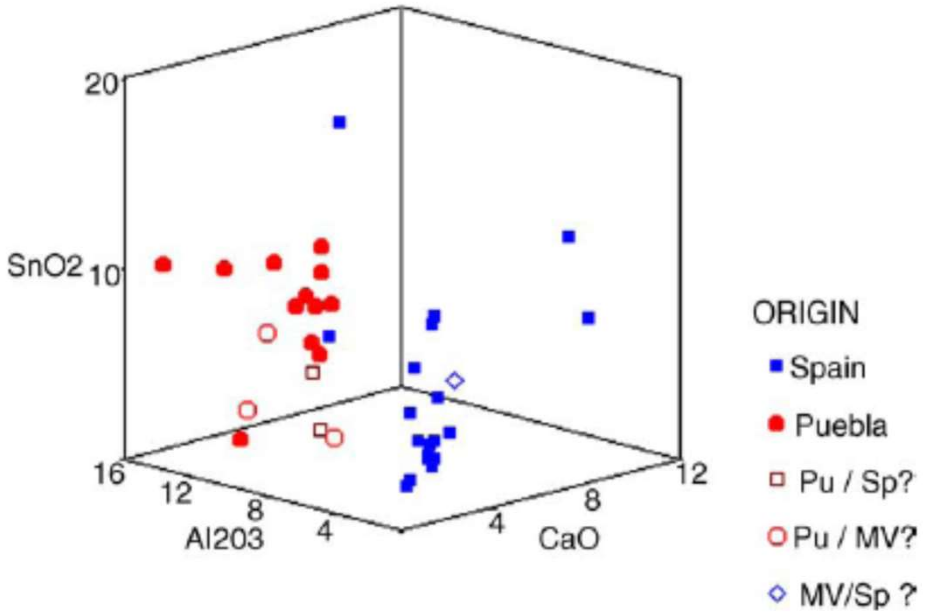
Quantitative analysis of glaze by XRF

- The thickness of the glaze must fully attenuate any signal originating from the underlying past





Spanish and Puebla white glaze



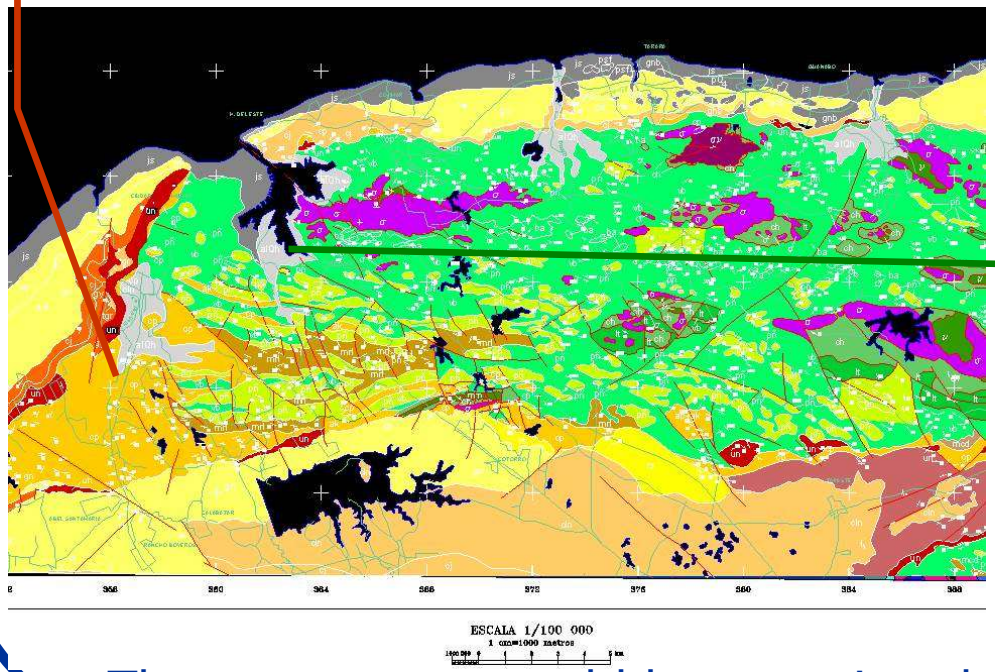
Puebla glazes exhibit a larger proportion of Al

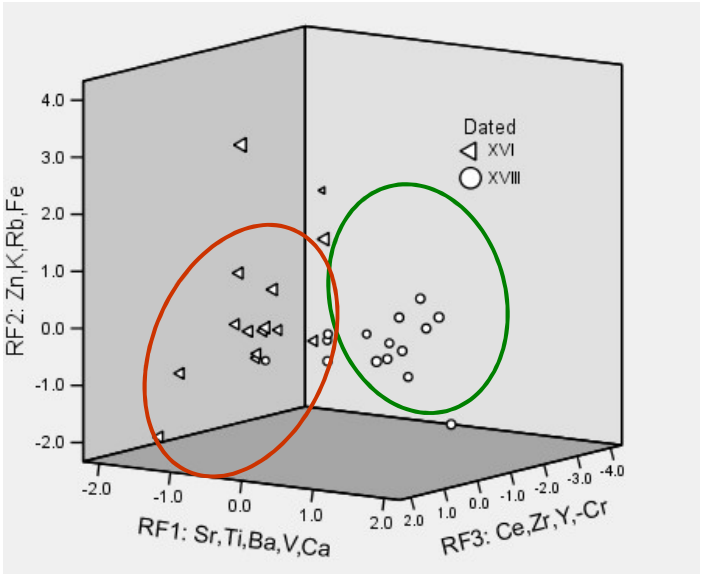
Probably made from fine clays as opposed to use of fine sand

Example 3: Cuban utilitarian ceramics by XRF

Example 3: Cuban utilitarian ceramics by XRF

Sand silt, siltstone, marga, grauwacka





Clear distinction by dating!

Limestone, limonite

The two groups could be associated to clay sources

Concluding remarks

- Compositional classification is an useful tool to support the verification or reformulation of diverse hypothesis in the characterization and effective conservation of cultural heritage objects
- No conclusive inferences can be made on the basis of compositional classification without an interdisciplinary effort
  - **DATA DOES NOT SPEAK BY ITSELF1**
- Interdisciplinary approach is unavoidable to achieve meaningful and comprehensive solution of questions

Concluding remarks

- Provenance studies require of sufficient data of comparable quality
- The goal can be achieved by using more than one approach, providing that the useful information is preserved

Thanks for your time and attention…