Example of a 3-Step Strategy PCA-PLS-LDA with Archaeometric Data: Identification of an Organic Material on a Neolithic Statuette

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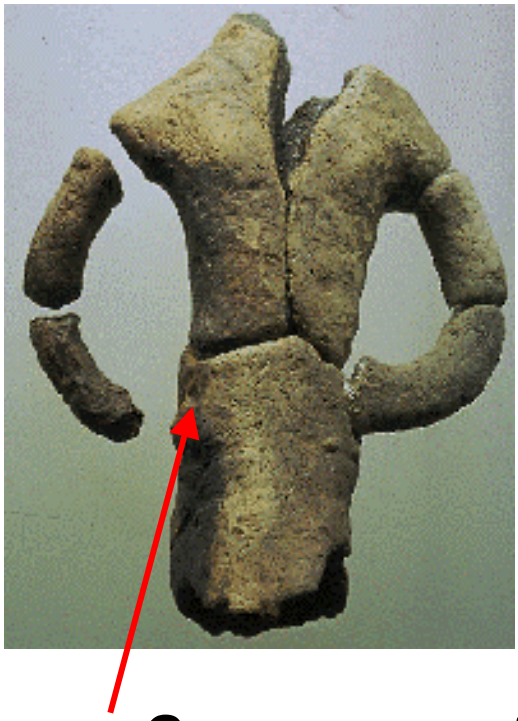
Overview

A terracotta statuette was found in a prehistoric settlement near Vienna (Austria).



^{14}C dating: 5650 - 5100 B.C.

Seven fragments

Preserved size	**14.2 cm**
Reconstructed size	**25 cm**

Prehistoric function

Maybe an idol (religious object)!
Maybe just a toy puppet?

Finding date 1989

Grooves were filled with an unknown dark material - obviously of organic origin.

First examinations of the dark material and experiences with similar material found on other archaeological findings - for instance the Neolithic *Tyrolean Iceman* - lead to the idea

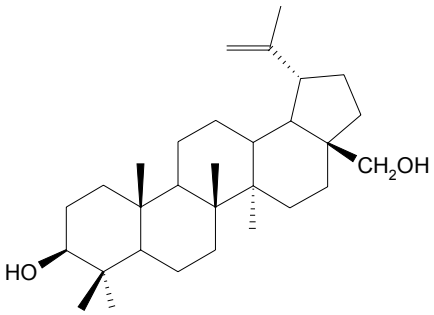
The dark material might be pitch produced by pyrolysis of birch wood.

Aim of the work was to evaluate this idea by chemotaxonomy + chemometrics.

Methods and Data

Compounds

Wood pitches can be characterized by **concentration patterns of triterpenoids**, such as *betulin* (characteristic for birch trees), or *friedelin* (characteristic for cork oak trees), and many others [1].



betulin

Samples

Reference samples were prepared by pyrolysis of wood and/or bark taken from four species of trees of the family *Betulaceae*.

Chemical Analysis

(1) A triterpenoid fraction was obtained by Kugelrohr distillation, followed by solid phase extraction [2].

(2) GC/MS analysis: on-column injection, DB5 30m, 25°C/min to 260 °C, 1.5°C /min to 290°C; electron impact ionization.

(3) Identification of main compounds by spectral similarity search.

(4) Characterization of 183 compounds by their mass spectra and retention indices, and determination of their relative concentrations.

(5) Selection of 50 compounds with maximum variance in their concentrations.

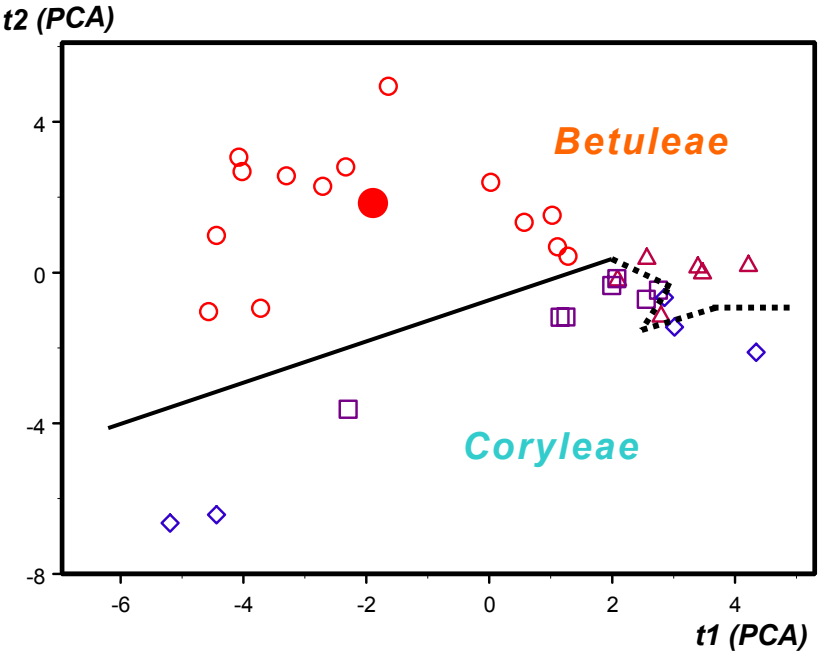
Data

33 objects (samples)	14	from *Betula*	(birch)	class 1	] tribe *Betuleae*
	6	from *Alnus*	(alder)	class 2	
	7	from *Corylus*	(hazelnut)	class 3	] tribe *Coryleae*
	5	from *Carpinus*	(hornbeam)	class 4	
	1	archaeological sample (unknown)			

50 features (relative concentrations, autoscaled)

PCA and HCA

PCA Principal Component Analysis Mapping

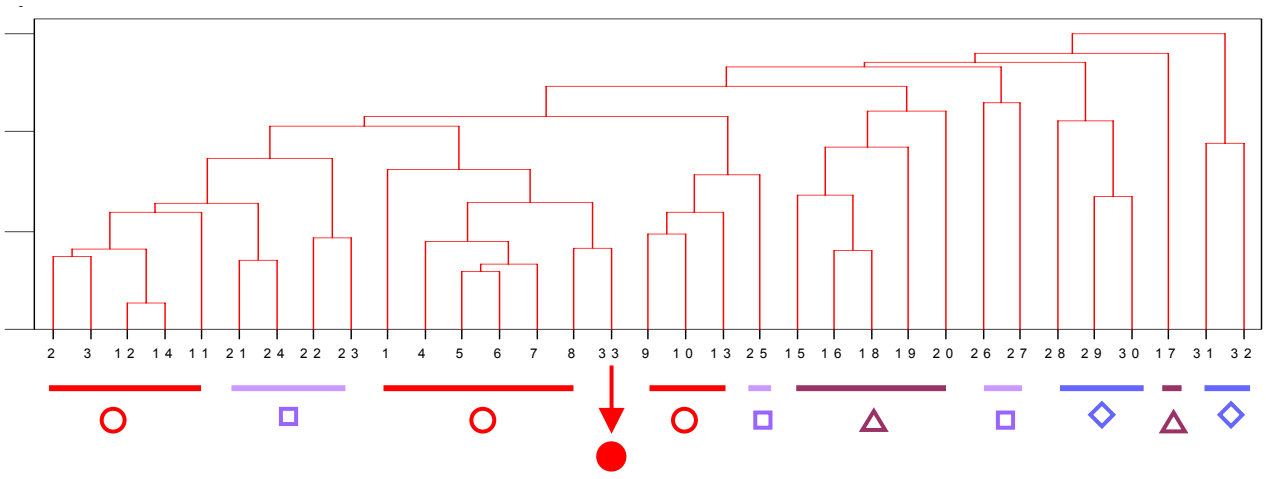


t1, *t2* are scores of PC1 and PC2, respectively, with variances 18.4 and 11.7% of total variance.

Separation of the tribes ***Betuleae*** (including *Betula* ○ and *Alnus* △), and ***Coryleae*** (including *Corylus* □ and *Carpinus* ◇).

● unknown material

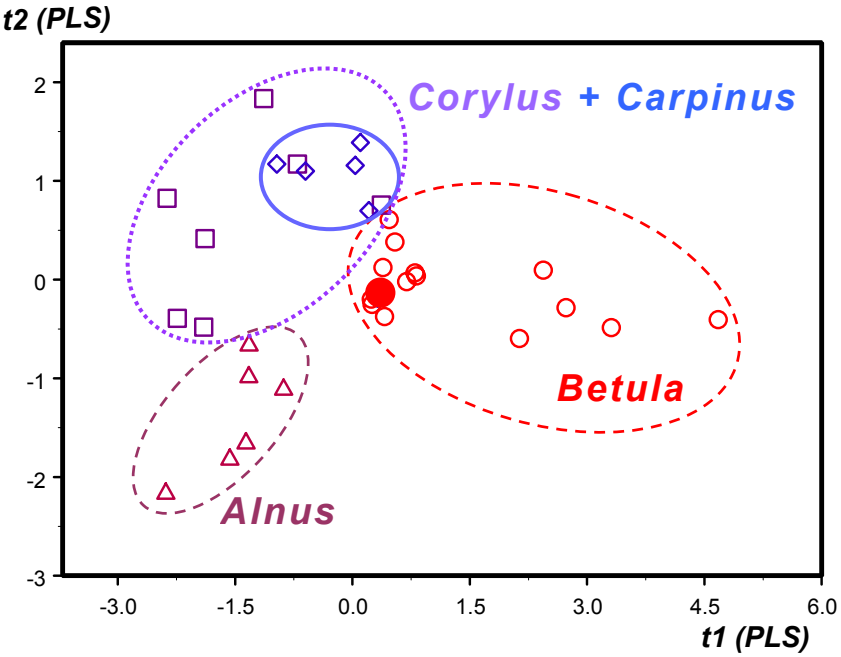
HCA Hierarchical Cluster Analysis



Similar clustering as obtained with PCA, however, less evident.

PLS and LDA

PLS Partial Least Squares Discriminant Mapping



t1, *t2* are *x*-scores of 1st and 2nd PLS component.

X: 50 concentrations

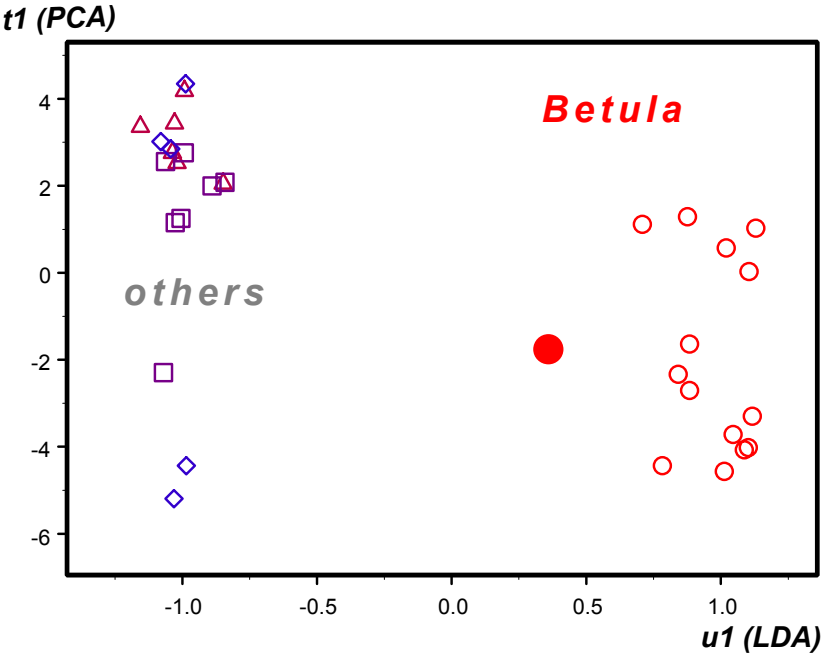
Y: 4 binary class variables

PLS: eigenvectors of

$$X^T Y Y^T X$$

Genus *Betula* is separated from genus *Alnus* and the overlapping genera *Corylus* and *Carpinus*.

LDA Linear Discriminant Analysis Mapping



u1 is the LDA discriminant variable, calculated from the first 25 PCA scores (for discrimination of genus *Betula* from the other classes).

t1 is the score of PC1.

Genus *Betula* is well separated from the other classes.

The unknown ● can be assigned to class ***Betula***.

Conclusions and References

The results strongly indicate that

The dark material from the Neolithic statuette was prepared from wood or bark of birch trees (*Betula*).

This conclusion is consistent with other finds in prehistoric Europe. Pitch made from birch trees has been used as a multifunctional material (as coating of pottery, as glue, even as gift).

The investigated pitch from the statuette may have been used to fix some textile dressing.

References

[1] Sauter F., Jordis U., Graf A., Werther W., Varmuza K.:
ARKIVOC, **1** [5], 735-747 (2000), electronic journal with free access
http://www.arkat.org/arkat/journal/Issue5/ms0074/ms0074.pdf
Studies in organic archaeometry I: Identification of the prehistoric adhesive used by the Tyrolean Iceman to fix his weapons.

[2] Sauter F., Varmuza K., Werther W., Stadler P.:
ARKIVOC **2002** [1], 54-60 (2002), electronic journal with free access
http://www.arkat-usa.org/ark/journal/2002/General/1-343E/343E.pdf
Studies in organic archaeometry V. Chemical analysis of organic material found in traces on a Neolithic terracotta idol statuette excavated in Lower Austria.

[3] Varmuza K.: **Projects in archaeometry** (Laboratory for Chemometrics)
http://www.lcm.tuwien.ac.at/pr/arch/

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