The Tyrolean Iceman

Origin of Wood Pitches Used as Adhesives on Prehistoric Tools and Weapons

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Abstract

In September 1991 a well conserved frozen mummy of a Late Neolithic man has been discovered in a glacial field near the Austrian-Italian border. This approximately five thousand year old *Tyrolean Iceman* (nicknamed *Ötzi* because found in the Ötztaler Alps) has been the subject of several studies [1, 2]. Together with the mummy several clothes, tools, and simple weapons were discovered. Typical for prehistoric stone-made tools and weapons is pitch (prepared by pyrolysis of wood or bark) used to glue the blades to their shafts [3]. Aim of this work was to identify the species of tree, which was used in prehistoric time to prepare this glue, by comparison with other relevant archaeological samples and with model pitches prepared from various trees.

Archaeological and recent pitches have been characterized by the relative concentrations of triterpenoids and related compounds measured by GC/MS. A set of compounds exhibiting the highest variances have been selected for multivariate data interpretation. PCA gave evidence that the Ötzi samples are pitches produced from birch barks. PLS discriminant mapping and linear discriminant classification confirmed this result and indicated the triterpenoids responsible for the different types of trees.

The applied multivariate chemotaxonomic approach indicated a close relationship between adhesive material from Ötzi´s tools with corresponding materials that have been found in archaeological samples from Northern and Central Europe.

[1] Spindler, K.; Wilfing, H.; Rastbichler-Zissernig, E.; zur Nedden, D.; Nothdurfter, H. (eds.): *Human mummies: a global survey of their status and the techniques of conservation.* Springer, Wien (1996).

[2] Höpfel, F.; Platzer, W.; Spindler, K.: *Der Mann im Eis, Band 1.* Veröffentlichungen der Universität Innsbruck, Bd. 187 (1992).

[3] Sauter, F.; Hayek, E.; Moche, W.; Jordis, U.: *Z. Naturforsch.* **42c**, 1152 (1987).

Introduction

Historical Background

-3300	An approximately 45 year old man died at an altitude of 3200 m in the mountains which are today called ***Ötztaler Alps***. He was well equipped with warm clothes, food, tools and weapons.
1991 09 19	The mummy was accidentally found by two German tourists. The body was partly covered by snow and ice.
1992 09 23	Austrian scientists and police recovered the mummy together with accompanying findings. Soon it became clear that the ***Tyrolean Iceman*** was from the Late Neolithic; he was nicknamed ***Ötzi***. The Tyrolean Iceman was conserved at the University of Innsbruck and was the subject of many scientific projects as well as of speculations. Exact measurements of the Austrian-Italian border resulted that the finding site of Ötzi is on Italian territory.
1998 01 17	Ötzi was transported from Innsbruck to Bolzano/Bozen in Italy (South Tyrol) and was put on public display.

Aim of this Work

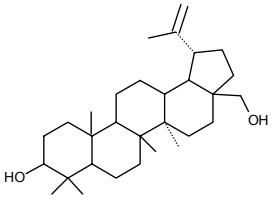
Wood pitch **(German: Holzpech, Dutch: houtpek ?) has been found on tools and weapons used by Ötzi. As in other prehistoric stone-made tools the wood pitch has been used to glue the blades to their shafts.**

Aim of the project was to *identify the species of trees* from which material was used to prepare this glue.

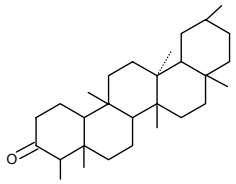
Data Generation

Compounds for chemotaxonomy

Wood pitch samples have been characterized by their relative concentrations of ***triterpenoids***. These compounds are relative stable during thermic treatment or give characteristic degradation products. Examples are



BETULIN: C_{30} H_{50} O_2, mw 442
typical for barks from birch trees



FRIEDELIN: C_{30} H_{50} O, mw 426
typical for oak trees

Samples

Three pitch samples from materials (axe, arrow) found near Ötzi;

prehistoric pitch samples and recent pitch and tar samples from different woods and barks produced by a standard pyrolysis procedure in the laboratory.

Chemical analysis

1. Kugelrohr distillation of 0.05 to 0.5 g samples.
2. Triterpenoid fraction is cleaned by solid phase extraction, finally resulting in 8 ml THF solution.
3. GC/MS analysis: on column injection, DB5 30 m, 25 ^{o}C/min to 260 ^{o}C, 1.5 ^{o}C/min to 290 ^{o}C; electron impact MS.
4. Evaluation of **GC/MS** data by library search, manual and software-supported comparison of spectra.
5. Semi-quantitative determination of 183 compounds in the triterpenoid region. Compounds were characterized by mass spectrum and retention index; some could be identified.

Data preprocessing and selection

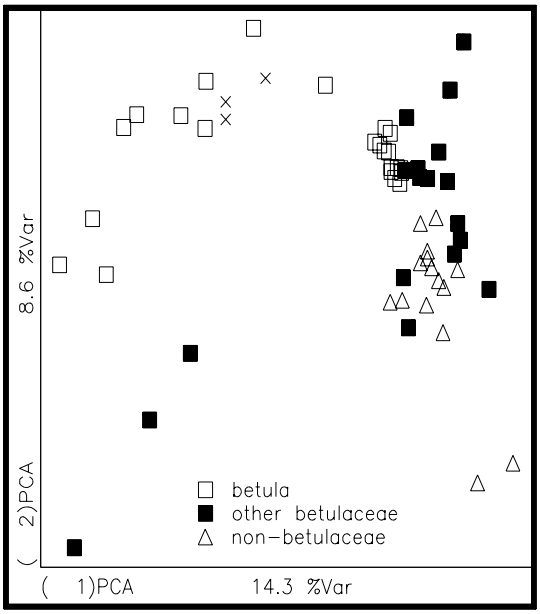
Normalization to equal sum of all 183 compounds. Selection of 50 features with maximum variance. Preprocessing and feature selection has been performed for each data set separately (in classification methods the Ötzi samples have been considered as unknowns).

Data Evaluation 1

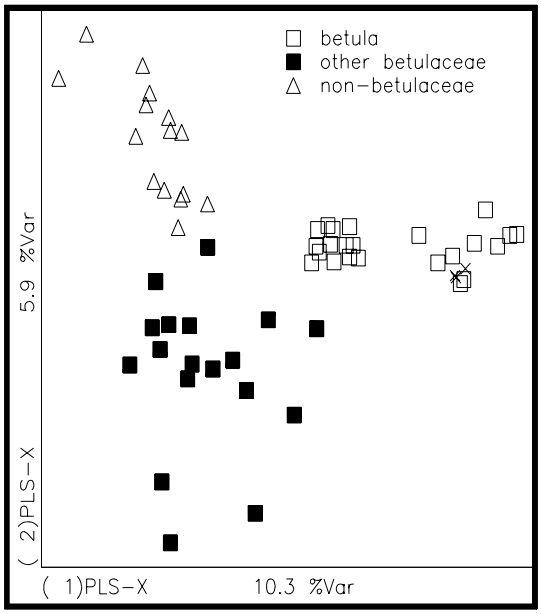
Previous investigations of other prehistoric materials guided to the hypothesis that also the wood pitch found with Ötzi may has been produced from birch-like trees (*betulaceae*). Birch tree (*betula*) is a sub-group (genus) from *betulaceae*.

Samples	3	Ötzi samples (**X**)
	23	birch tree samples (*betula*)
	18	samples from other *betulaceae*
	15	samples from non-*betulaceae* (oak tree and others)
Features	**X:** autoscaled; **Y:** 3 binary variables according to the 3 tree classes (for PLS)	

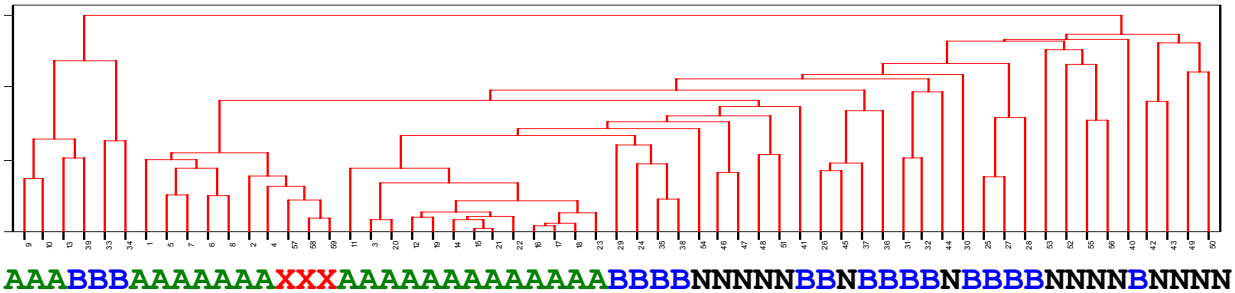
PCA



PLS



HCA



AAABBBAAAAAAAXXXAAAAAAAAAAAAAABBBBNNNNNBBNBBBBNBBBBNNNNBNNNN

A: betula (birch trees) **B**: other betulaceae **N**: non-betulaceae **X**: Ötzi samples

PCA, PLS and HCA confirmed the hypothesis that the Ötzi samples belong to the group *betulaceae*, probably to the subgroup *betula* (birch trees).

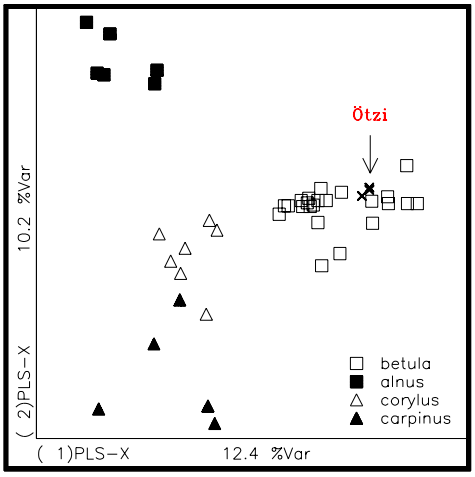
Data Evaluation 2

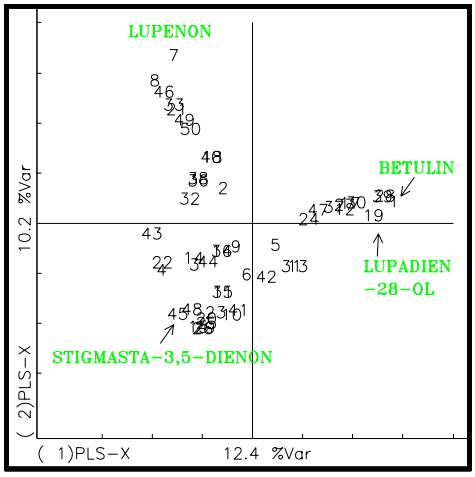
In the next step the reference data were restricted to samples from the group ***betulaceae***. PLS discriminant analysis was applied to obtain information which subgroup of trees best corresponds to the Ötzi samples.

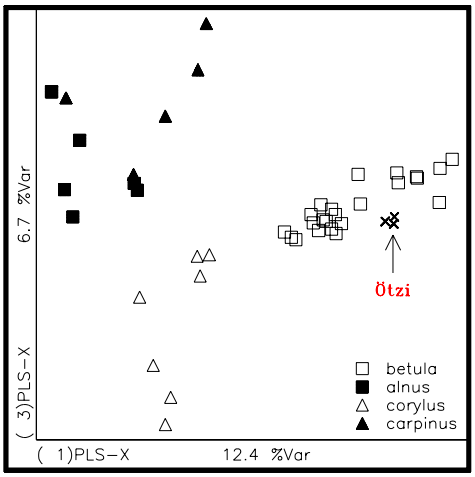
Samples	3	Ötzi samples	X			
	23	birch tree (*betula*)	□	7	hazelbush (*corylus*)	Δ
	6	alder (*alnus*)	■	5	hornbeam (*carpinus*)	Δ

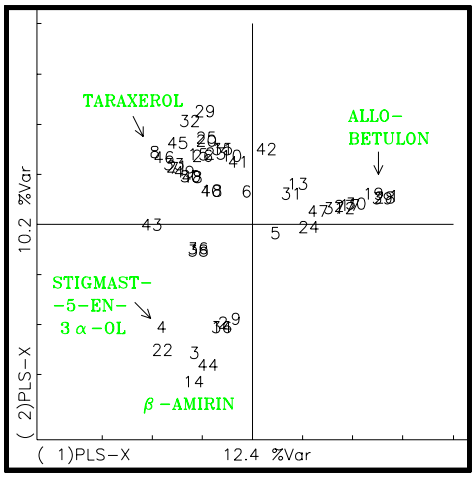
Features **X:** autoscaled; **Y:** 4 binary variables according to the 4 classes

PLS Score plots (left) and loading plots (right) for first three x-components









The data structure conserving PLS discriminant analysis is appropriate for this four-class problem. The classes are well separated when the first 3 PLS x-components are considered.

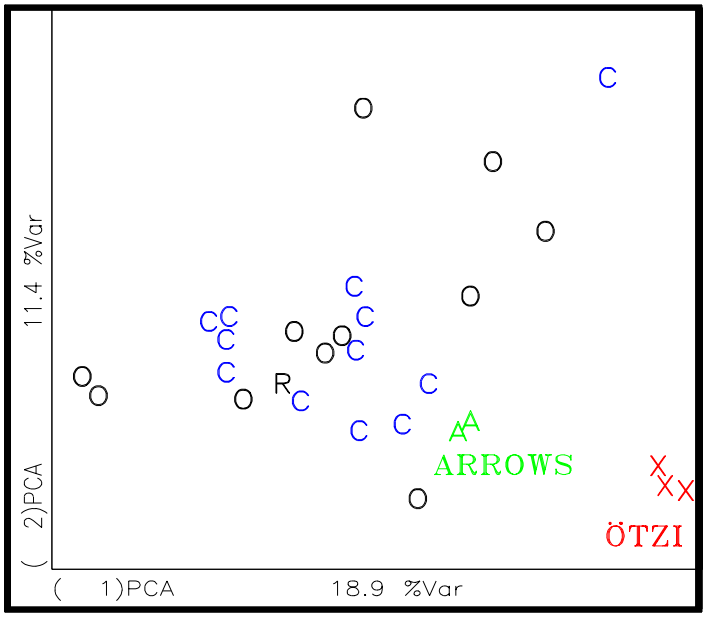
PLS discriminant analysis gave clear evidence that the Ötzi samples belong to the subgroup *betula* (birch tree).

Data Evaluation 3

The Ötzi samples have also been compared with other prehistoric wood pitch samples. Additionally, a wood pitch sample has been considered that has been recently produced by simple methods as probably available in former times.

Samples	3	Ötzi samples	**X**
	12	samples from *coatings* on pottery and wooden boxes (Jutland/Denmark, Lower and Upper Austria)	**C**
	2	samples from *arrow heads* (Copper Age, Mondsee/Upper Austria)	**A**
	11	*other* prehistoric pitch samples	**O**
	1	*recently* produced pitch sample	**R**

PCA



Pitch used as coating is different from those used as adhesive.

The recently produced pitch sample is similar to prehistoric coating.

The Ötzi samples are similar to the pitch samples found on arrow heads which have approximately the same age but have been found some hundred km away.