

# Archaeometry by GC/MS-Chemometrics: Origin of Wood Tar Pitches used by the *Tyrolean Iceman*

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# Introduction

1991 the mummy of a prehistoric man was found on a glacier at an altitude of 3200 m at the frontier between Tyrol (Austria) and South Tyrol (Italy).

As this Alpine region is called „Ötztaler Alps“, the „Tyrolean Iceman“ was nicknamed

*Ötzi*

He lived some 5200 years ago in the Late Neolithic (Chalcolithic) and - having been deep-frozen - he as well as the objects found with him were well preserved.

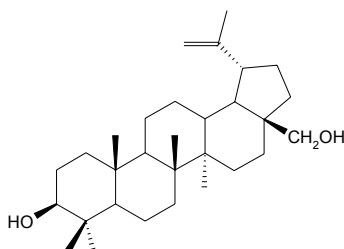
Among his weapons were flint-stone arrowheads and a copper hatchet, all of them fixed to their shafts by pitch, used as agglutinant.

**Aim of the present investigation  
was to identify from which species of trees  
this glue was made in prehistoric times.**

# Data Generation

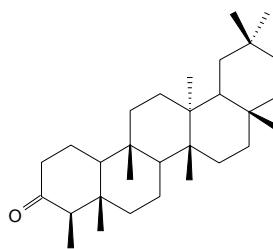
## Compounds for Chemotaxonomy

Wood pitches can be characterized by terpenoid components; those made from broad-leaved trees by triterpenes, such as



Betulin

characteristic for birch trees



Friedelin

characteristic for cork oak trees

## Samples

Prehistoric samples were taken from arrowheads and from the copper hatchet.

Reference samples were prepared by pyrolysis of wood and/or bark taken from various species of trees.

## Chemical Analysis

- 1. Isolation and purification of the triterpenoid fraction:**  
Kugelrohr distillation, followed by solid phase extraction.
- 2. GC/MS analysis:**  
On-column injection, DB5 30m, 25°C/min to 260°C, 1.5°C/min to 290°C, electron impact MS.
- 3. Evaluation of GC/MS data:**  
Library search and software-supported spectra comparison.
- 4. Semi-quantitative determination and chemometrics:**  
183 compounds in the triterpenoid region, characterized by MS and retention index, have been determined. Relative concentrations of 50 most relevant compounds (maximum variance) have been used for multivariate data analysis.

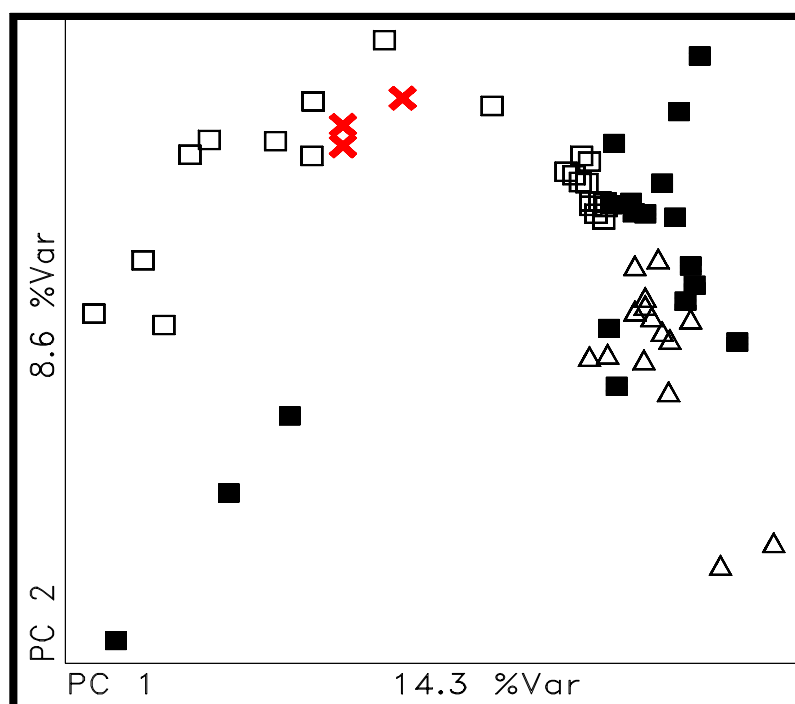
## Question No 1:

### Family of birch trees (*Betulaceae*) or any other trees ?

Previous investigations of other prehistoric materials lead to the hypothesis that the wood pitch found with *Ötzi* may also have been produced from birch-like trees (*Betulaceae*).

<b>Samples</b>	3	<i>Ötzi</i> samples	X
	23	birch tree samples ( <i>Betula</i> )	□
	18	samples from other <i>Betulaceae</i>	■
	15	samples from non- <i>Betulaceae</i> (oak tree and others)	△
<b>Features</b>	autoscaled		

#### Principal Component Analysis Plot (PCA Plot)



**Principal component analysis showed that the *Ötzi* samples belong to the family *Betulaceae*, probably to the genus *Betula*.**

## Question No 2:

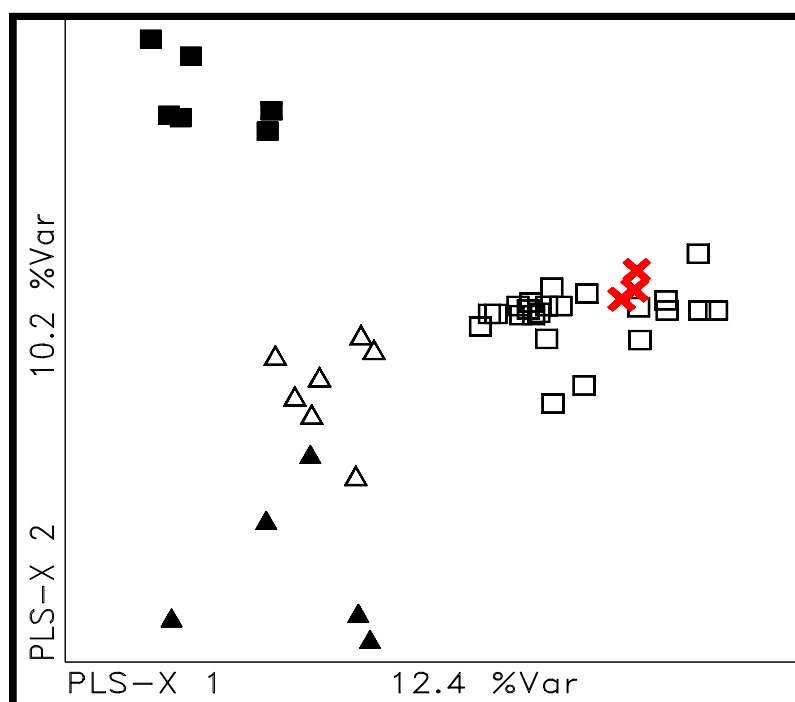
### Birch (*Betula*) or any other member of the birch family (*Betulaceae*) ?

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

**Samples**    3 *Ötzi* samples    **X**  
                  23 birch tree (*Betula*)    □    7 hazelnut (*Corylus*)    △  
                  6 alder (*Alnus*)    ■    5 hornbeam (*Carpinus*)    ▲

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

#### Partial Least Squares Discriminant Analysis Plot (PLS Plot)



**PLS discriminant analysis gave evidence that the *Ötzi* samples belong to the genus *Betula* (birch tree).**

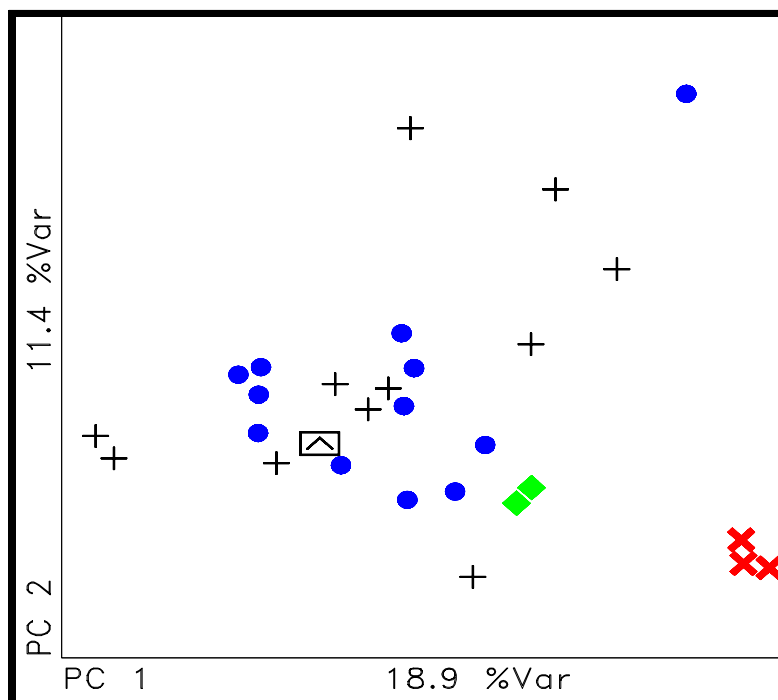
### Question No 3:

## Were different pitches used for particular applications ?

The *Ötzi* samples have been compared with other prehistoric pitches used for different purposes.

Samples	3	<i>Ötzi</i> samples	X
	12	pitches from <b>coatings</b> on pottery and wooden boxes (Denmark, Lower and Upper Austria)	●
	2	pitches from <b>arrowheads</b> (Copper Age, Mondsee/Upper Austria)	◆
	11	<b>other</b> prehistoric pitches	+
	1	pitch <b>recently produced</b> in a charcoal pile	⊠

### Principal Component Analysis Plot (PCA Plot)



- Pitches used for coatings are somewhat different from those used for adhesives.**
- A pitch sample recently produced in a charcoal pile corresponds to pitches taken from prehistoric coatings.**
- The *Ötzi* samples are similar to pitches from Upper Austria found on arrowheads of the same time.**

# Conclusions

**The agglutinants used by *Ötzi*  
to fix his weapons were made from  
bark of the birch tree  
(*Betula verrucosa*).**

**It is possible that different technologies  
have been applied in prehistoric times  
to prepare the pitches  
dedicated for particular purposes.**

**Appropriate analytical techniques  
followed by chemometrics  
were important to obtain these conclusions.**

See also publication

**Sauter F., Jordis U., Graf A., Werther W., Varmuza K.:  
*ARKIVOC*, 1, [5] 735-747 (2000)**

**Studies in organic archaeometry I: Identification of the  
prehistoric adhesive used by the “Tyrolean Iceman” to  
fix his weapons.**

*ARKIVOC* is an electronic journal with free access:  
<http://www.arkat.org/arkat/journal/Issue5/ms0074/ms0074.pdf>

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