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ARCHAEOMETRY OF BIRCH BARK PITCH

During the last decades, archaeologists became increasingly interested in birch bark pitch (BBP; German: »Birkenrindenpech«), as traces of this material were more frequently excavated. The present paper is, therefore, giving an overview of the chemical nature of BBP, the most important applications of it in prehistoric times, where and in which prehistoric periods BBP is mainly discovered, the chemical methods used to identify an organic, pitch-like find as BBP and (based on our long-time experience) which one of these analytical methods we consider as the most effective one[1].

Frequent misunderstandings stimulate some introductory remarks regarding the terminology: what here is dealt with is a pitch (German: »Pech«) and not a resin (German: »Harz«), which mainly means the natural sticky exudate produced by trees to cap an injury. But »urn resins« (German: »Urnenharze«) is an antiquated denomination for – probably, but not analysed – BBP. BBP is in its chemical nature also totally different from dark natural asphalt and natural highly viscous tar (German: »[Natur]Asphalt«), as it was used, e.g., in ancient Mesopotamia for various purposes. It is not identical with artificially prepared tar (German: »Teer«), but is related to it regarding its chemical components. A pitch (such as BBP) is thermoplastic, but practically solid at room temperature and is and was prepared via the intermediate of a tar, which is highly viscous, but liquid (and can, therefore, be used, e.g., as cart grease).

When in the last decades traces of pitch-like organic matter were more frequently excavated the wish for even more analytical methods arose, which should allow an unambiguous identification as BBP. Therefore, some organic chemists working in archaeometry intensified their efforts to improve such specialised analyses, although this had to be done with only tiny quantities and although they were well aware that such samples are always encompassing a multitude of different chemical compounds, thus making all research work in this field rather time-consuming.

Mainly the latter aspect was and is a major problem for many specialists working in organic chemistry, as most of them can deal only casually with archaeometrical topics as an ancillary activity.

Nevertheless, in the course of time, such a remarkable number of papers appeared on this topic that even a review on BBP archaeometry was published by J. Weiner already in 1999. Of course, up to now, many more authors of papers could be added as well as even whole research groups working for some time on such topics. Among the latter, we would like to mention in particular the BBP specialised teams of K. Ruthenberg (1997) and of J. Koller (Koller/Baumer 1993; 1997).

PREPARATION OF BIRCH BARK PITCH

Under laboratory conditions BBP can easily be prepared from dried bark of birch (*Betula pendula = B. alba = B. veruccosa*) by smouldering (i.e. heating under exclusion of free access of air) beginning at about 200-250 °C, thus producing a characteristically smelling dark tar. When this is later heated to slightly higher temperatures, more of the volatile components are evaporated and a pitch is obtained as a thermoplastic dark material, comparable in its behaviour to asphalt as is used for road surfacing. For the production of pitches from various trees (needed for distinctions as well as for production of reference samples), our team worked out a routine method (described in detail below; Sauter et al. 2000).

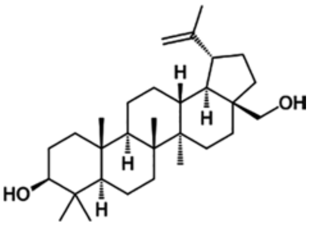

Fig. 1 Betulin. – (After V8rik at en.wikipedia [https://commons.wikimedia.org/wiki/File:Betulin.svg], »Betulin«, https://creativecommons.org/licenses/by-sa/3.0/legalcode [9. 1. 2019]).

Fig. 2 Sopron »Burgstall« (Kom. Győr-Moson-Sopron / H), tumulus 89. Hallstatt pottery glued in antiquity. – (Photo L. Puchinger).

CHEMICAL NATURE OF BIRCH BARK PITCH

All these pitches are rather complex mixtures encompassing a multitude of organic compounds, many of them being terpenes, which allow to distinguish pitches made from conifers from those made from deciduous trees. For BBP, in particular, the most important terpene is the pentacyclic betulin (**fig. 1**; Hayek et al. 1989a), which occurs in nature in high percentage in the external bark layers of the birch tree, thus being the cause for its characteristic white colour. Although at first glance a substance of this formula might look decomposable, it is rather stable and if it is present in BBP in high concentration it can be considered as one of BBP's most important marker compounds.

Specialists working in experimental archaeology in order to study an assumed prehistoric production of BBP (e. g. Kurzweil / Todtenhaupt 1991; in Berlin's Museumsdorf Düppel) applied various methods, e. g., using simplified structures related to charcoal piles. At any rate, it is obvious that the chemical composition of products produced by different methods can vary considerably from each other.

USE OF BIRCH BARK PITCH IN PREHISTORIC TIMES

The reason why BBP shifted so much into the focus of interest of archaeologists is that it was used in prehistoric times – mainly because of its thermoplastic, asphalt-like character – for a rather large spectrum of practical applications:

- a glue to repair broken pottery (Charters et al. 1993); see as an example an early Iron Age sherd repaired by BBP from Sopron »Burgstall« (Kom. Győr-Moson-Sopron / H), tumulus 89 (**fig. 2**);
- a glue to fix a metal hatchet to its shaft (Sauter et al. 2000; Sauter / Jordis / Hayek 1992; Hayek et al. 1991);
- a glue to fix flint arrowheads to their shafts (Sauter et al. 2000; Sauter / Jordis / Hayek 1992; Hayek et al. 1991);
- a glue to fix Iron Age clay statuettes to their (decayed, probably wooden) bases (Sauter et al. 2002a);
- a glue to fix (assumed) textiles to an Early Neolithic terracotta Venus statuette (Sauter et al. 2002b);

– a glue to fix ornaments (made from different materials, e. g. Sauter/Rossmanith 1967) to the outside of pottery (reported by archaeologists but without chemical analysis);
– a glue to fix caps to transport amphorae (reported by archaeologists but without chemical analysis);
– an embellishing black shiny layer on the outside of pottery (e. g. Sauter 1967);
– a layer applied to pottery to make it impermeable to water (e. g. Sauter 1967);
– a gift offered ritually upon thermal destruction (due to its value, which was raised by transport) (Sauter/Jordis/Hayek 1990-1992);
– a matter used ritually as a substitute for frankincense (reported by archaeologists, but without chemical analysis).

WHERE AND FROM WHICH TIMES BIRCH BARK PITCH WAS FOUND

Up to now samples of BBP which were excavated and also chemically identified stem mainly from European countries like Austria, the Czech Republic, France, Germany, Poland, and the United Kingdom. Occasional finds of prehistoric BBP are reported even from Mediterranean regions (Binder et al. 1990), and of course BBP is also discovered in northern countries (Hayek et al. 1989b) where the birch was and is by far more common (this giving reason to consider a conceivable transport route, a »Birch Pitch Road« in analogy to the famous »Amber Road«). The border zone of BBP towards the East and the South is in discussion.
A remarkable part of chemically analysed BBP samples are dated from Neolithic (Sauter et al. 2000; 2002b; Binder et al. 1990) to Hallstatt (e. g. Sauter 1967) times. Less frequently found but of particular interest is BBP from Palaeolithic (Koller/Baumer/Mania 2001; Grünberg 2002) and Mesolithic (Maglemosian) (Aveling/Heron 1998) sites: BBP can thus be considered as the eldest synthetically produced organic substance in the world, maybe outnumbered only by alcohol. The latest chemically identified troves of BBP are Roman (Charters et al. 1993).

HOW BIRCH BARK PITCH MAY HAVE BEEN APPLICATED IN PREHISTORIC TIMES

For all sorts of prehistorical application, BBP had to be warmed up cautiously from the solid to a tarry state. In contrast to the straightforward use as agglutinant, the production of a thin and shiny layer on pottery is more elaborate, although on potsherds with such a layer sometimes structures can be found which really show an appearance as if they were brush marks.
But attempts to apply molten BBP by means of a brush to the pottery end quickly in the solidification of the highly viscous tar. The (theoretical) possibility to reach a more liquid state of BBP by heating it up to an even higher temperature is more than risky, as thermal decomposition can readily occur. Based on trials we consider a smooth rubbing of a lump of BBP at the surface of the heated pottery. Indeed, not only the desired black layer can thus be obtained, but also the misleading »brush marks«.

ANALYTICAL METHODS TO IDENTIFY PREHISTORIC BIRCH BARK PITCH

Historic efforts

The first approaches to identify BBP where rather straightforward: heating BBP gave a characteristic odour reminding of that occurring when birch bark is heated – although this »analysis« was somewhat primitive,

the result was correct. The first real chemical approach was done by W. Sandermann (1965), a German wood specialist, who (influenced by the Danish ethnography) realised a conformance when he compared the spectra of extracts of prehistoric BBP and of birch bark, but he missed to publish comparisons which would exclude other trees.
A different approach was chosen by H. Funke (1969). He isolated by chemical means betulin from prehistoric BBP: an efficient method, but needing large quantities of the archaeological material.

Identification by ^{13}C-NMR Spectroscopy

As said above a detection of the marker substance betulin indicates that the sample in question stems from the birch-like family (*betulaceae*), while a high percentage of betulin with high probability points out that the birch itself was used as the starting material. The ^{13}C-NMR Spectroscopy method could be applied effectively even to small quantities of the samples. Experimental details are given in various studies (Fröhlich et al. 1999; Sauter et al. 2001).

Chromatographic methods

Many authors use(d) directly High-Performance Liquid Chromatography (HPLC) or Gas Chromatography (GC), both being efficient methods, bearing only a problem: one always has to deal with also a large number of ambiguous components which are not characteristic of distinction purposes. This is true for prehistoric BBP as well as for laboratory-made samples of reference pitches. Some authors used such methods combined with, e. g., Mass Spectrometry (MS) or GC (Koller/Baumer 1997).
For our own studies (Sauter et al. 1987) we optimised this method by stepwise concentration of the sample: firstly by *Kugelrohr* (bulb-to-bulb) distillation under reduced pressure, followed by distillation (under reduced pressure) of the characteristic triterpene fraction (These concentrations are omissible in analyses done by pyrolyser, cf. below). The pitch thus obtained is then analysed by GC-MS, i. e., separated (mainly) by GC into single components, which then are identified by MS.
To distinguish BBP from pitches prepared from other species of wooden plants a lot of comparisons had to be carried out: Firstly reference pitches were prepared via the mentioned thermolysis procedure (e. g. by bulb-to-bulb distillation) from a large variety of bark and/or branches of conifers as well as of deciduous trees, all of them, of course, well-defined by a botanist. Additionally, reference pitches from different species from the birch family (*betulaceae*) were also prepared.
Table 1 names those common trees which were incorporated into our studies in order to allow a doubtless analytical distinction of the birch from other trees which might have been used in prehistory as starting material for the preparation of a pitch.
By some studies of this kind using a commercial computer-based spectra-comparing system (INCOS) we could identify c. 20 compounds, all of them chemotaxonomically related, belonging only to the »betulin family« (e. g. lupeol, lupeone, etc.).
Of course BBP samples taken from different excavated objects can vary considerably from each other, firstly because different starting materials were maybe used (e. g. by mixing some wooden parts to the bark), secondly because of differing production conditions (e. g., different temperatures applied, differences in the degree of O_2 exclusion) and thirdly because of maybe differing conditions in the ground prior to excavation.

Tab. 1 List of the trees from which the pitches were analysed.

deciduous trees		coniferous trees	
alder	*Alnus glutinosa*	black pine	*Pinus niger*
birch	*Betula pendula*	blue spruce	*Picea pungens*
European beech	*Fagus sylvatica*	pine	*Pinus sylvestris*
hazel	*Corylus avellana*	silver fir	*Abies alba*
hornbeam	*Carpinus betulus*	spruce	*Picea abies*
oak	*Quercus robur*		
willow	*Salix caprea*		

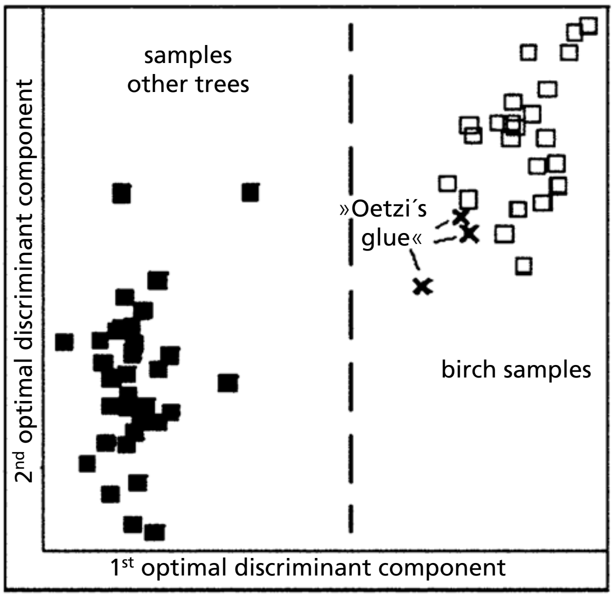

Fig. 3 The Principal Component Analysis (PCA) shows that the »Ötzi samples« can be attributed to samples made from the birch and not to samples made from a variety of other trees. – (After K. Varmuza / W. Werther in: Sauter et al. 2000, fig. 2).

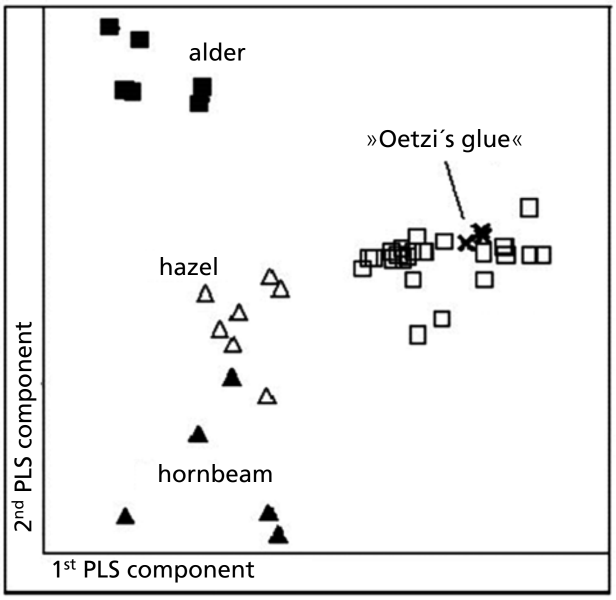

Fig. 4 Partial Least Square Discriminant Analysis (PLS-DA) shows that within a group of four deciduous trees the »Ötzi samples« belong to the birch (*betula*). – (After K. Varmuza / W. Werther in: Sauter et al. 2000, fig. 3).

Therefore, most of our GC-MS results were studied finally by chemometrics (Varmuza/Werther/Sauter 2001; Massart et al. 1997; Beebe/Pell/Seasholtz 1998; Varmuza 1998; Hayek et al. 1990), thus allowing a clear attribution to the botanical starting material, allowing even an unequivocal distinction within the members of the birch-like family (*betulaceae*).

Our chemometry studies on BBP are exemplified here by **figures 3** and **4** which in this special case show by cluster analysis the identification of the glue used by the famous »Tyrolean Iceman« (customarily nicknamed »Ötzi«) to fix his arrowheads and his hatchet to their shafts (Sauter et al. 2000).

IDENTIFICATION BY PYROLYSIS LINKED WITH GAS CHROMATOGRAPHY AND WITH MASS SPECTROMETRY

The method named in the headline (Glajch/Lubkowitz/Rogers 1979; Ingemarsson et al. 1998; Nilsson et al. 1999; Heck 1999; Karr/Comberati/Warner 1963) is also a chromatographic one, but is treated here as a special chapter, because according to our assessment it is the most effective technique for BBP analysis. It is based on pyrolysis (Py, thermal destruction) of the sample, here – differently to tar and pitch production – in

totally O_2-free atmosphere under well-defined heating conditions (such as temperature, rise of temperature, etc.), whereby the destruction products (pyrolysates) are transported by a stream of inert gas (N_2, He, etc.) through an adequately chosen gas chromatographic column.
Then these now (mainly) separated pyrolysates can be identified either by comparison of their retention times with those of expected from reference substances, or directly by MS, applying a commercial computer programme devised for substance identification.
Based on this method, we stepwise built up a sequence which we now mainly apply: Pyrolysis-Capillary Gas Chromatography (Py-CGC), usually linked with MS to Py-CGC-MS, preferentially followed by pattern recognition (chemometrics). Thus the desirable unequivocal assignment of very small amounts of BBP (down to even 0.1 mg of the pure sample of pitch) can be obtained.
As all analytical methods using MS also the Py-CGC-MS method offers the possibility to identify by a computer programme totally unexpected substances which might occur in a sample (or at least to detect their existence). Depending on the particular problem in question chemometric studies can also be very helpful (as mentioned above).
Having used Py-CGC also for some other topics (e. g. analyses of ancient parchments [Puchinger/Leichtfried/Stachelberger 2002], old lacquers and ancient dyestuffs [L. Puchinger and F. Sauter as Austrian Partners in EC Research Project »Med-Colour-Tech«, No. 0154046, co-ordinator Y. Karapanagiotis, Ormylia Art Diagnosis Center, Greece]) we dare to state that the pyrolysis-based analytical methods are advantageous not only because of their wide applicability but above all because of the tiny sample quantities needed – a necessity if museum exhibits should be analysed.

EXPERIMENTAL DATA

Valuable contributions to this topic were made by colleagues from related institutes (K. Varmuza, W. Werther, P. Krenmayr, H. Lohninger, A. Graf) and by five MSc theses and a PhD thesis within our team (E. W. H. Hayek, W. Moche, S. Leder, J. D. Schrattenecker, K. Dobrezberger).

Pyrolysis

All pitches were pyrolysed by a Double-Shot Pyrolyser PY-2020iD from Frontier Lab (working in free fall) in a cup filled with usually 1.4-1.7 mg of pitch sample. During pyrolysis, the temperature of the furnace is kept at 600 °C over a period of 1 min (these pyrolysis data were the optimised result of a series of varying conditions).
It was found out that under these conditions the main components of BBP were triterpenes including betulin, the characteristic marker substance for the birch tree (as mentioned above), with a retention time of c. 27 min by application of our optimised GC-oven heating programme.

Capillary Gas Chromatography – Mass Spectrometry

The analyses were carried out with a Thermo Trace GC Ultra Gas Chromatograph linked to a Thermo DSQ II Single Quadrupole Mass Spectrometer.

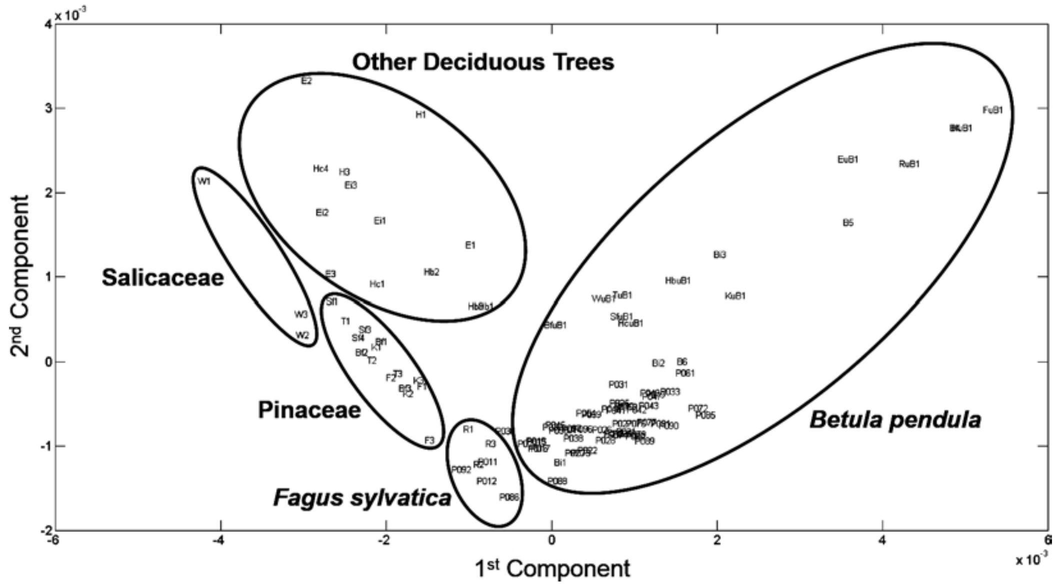

Fig. 5 The Principal Component Analysis (PCA) shows that the birch (*Betula pendula*) forms a cluster for its own, thus allowing to distinguish it from the great variety of other deciduous and pine family pitches. – (Illustration after Schrattenecker 2015, 83).

– Fused Silica Capillary Column DB-5MS (Agilent J & W), 15 m × 0.25 mm, film thickness 0.1 µm.
– Carrier gas: He; pressure (column head): 70 kPa.
– Split or Splitless mode; split/splitless injector temperature: 330 °C; transfer line temperature to MS: 300 °C.
– Multistage oven programme: 90 °C (2 min), 1st heating rate up to 200 °C (7 °C/min), 2nd heating rate up to 290 °C (4 °C/min), 3rd heating rate up to 340 °C (7° C/min), holding temperature: 340 °C (3 min).
– Xcalibur™ Software for the administration of GC-MS data.
– Ion source temperature: 250 °C; electron ionisation: 60 eV; positive ions, full scan 50-650.
– NIST mass spectrometry database.

Chemometrics

A multivariate classification method has been applied to the chromatographic data aiming to determine the class of the original material used for the preparation of the pitch. The data evaluation method applied was the Principal Component Analysis (PCA), carried out in Matlab R2013b. Previously, the retention times of all components had to be corrected, the relative peak abundance (intensity) calculated and the Savitzky-Golay filter used for signal processing filtering. Only then all measuring points of a pyrogram could be converted into a txt-file (tab-deliminated).
The last step was to insert the new data in the exdata matrix and to carry out statistical computation, producing as result a plot of the 1st versus the 2nd principal component (**fig. 5**).

Outlook on further studies

Future studies on BBP, in general, to be done will aim at simplifications of BBP analysis without reducing the accuracy when dealing with tiny sample quantities. Many samples more will have to be analysed to get

more insight into the most southern and most eastern sites where BBP was used in prehistory, as well as into some more materials to which BBP may have been applied.
Most important will be the question which other trees apart from the birch (*Betula pendula*) may also have been used in prehistoric times for the production of pitch; this the more, as some of our most recent but yet unpublished studies proved the additional use of a pitch prepared from the beech tree (*Fagus sylvatica*).

Notes

1) This articles figures as »Studies in Organic Archaeometry VIII«. Earlier papers in this series are (all accessed 11.12.2018):

F. Sauter / U. Jordis / A. Graf / W. Werther / K. Varmuza, Studies in Organic Archaeometry I: Identification of the prehistoric adhesive used by the »Tyrolean Iceman« to fix his weapons. Arkivoc 2000/v/7, 735-747. http://dx.doi.org/10.3998/ark.5550190.0001.507.

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Zusammenfassung / Summary / Résumé

Archäometrie von Birkenrindenpech
Birkenrindenpech ist ein dunkles organisches Material, das auf verschiedensten prähistorischen Funden, besonders auf Keramik, angetroffen wird. Die vorliegende Arbeit informiert über die chemische Natur von Birkenrindenpech, seine Herstellung, seine Verwendungsarten in prähistorischen Zeiten, in welchen Gegenden es zutage kommt, aus welchen Zeiten solche Funde stammen, welche chemische Analysemethoden bei Grabungsfunden zur Identifizierung als Birkenrindenpech verwendet werden, welche Methoden wir selbst angewandt haben und welche davon nach unserer Einschätzung vor allem bei Vorliegen nur kleiner Probemengen besonders vorteilhaft ist.

Archaeometry of Birch Bark Pitch
Birch bark pitch (BBP) is a dark organic matter which is found on various types of prehistoric objects, most frequently on pottery. The present paper informs what sort of substance it is, how it can be prepared, what it was used for in prehistoric times, in which regions it is found, to which prehistoric periods such finds can be assigned, which analytical methods can be used to identify an excavated sample as BBP, which ones were used by our own team, and which one of these is – according to our assessment – particularly advantageous regarding the generally low quantity of sample material.

Archéométrie de l'écorce de bouleau
Le brai d'écorce de bouleau est une matière organique foncée que l'on trouve sur divers artefacts préhistoriques, en particulier dans les céramiques. Le présent document informe sur la nature chimique du brai de bouleau, sa production, ses utilisations à l'époque préhistorique, dans quelles régions il a été découvert, d'où proviennent ces découvertes, quelles méthodes d'analyse chimique sont utilisées pour identifier le brai de bouleau dans les mobiliers, quelles méthodes nous avons utilisées et lesquelles sont particulièrement intéressantes pour notre méthode, surtout si seules de petites quantités d'échantillons sont disponibles. Traduction: L. Bernard

Schlüsselwörter / Keywords / Mots clés

Archäometrie / Birkenrindenpech / Pyrolyse / Gaschromatographie / Massenspektrometrie
Archaeometry / birch bark pitch / pyrolysis / gas chromatography / mass spectrometry
Archéométrie / brai de bouleau / pyrolise / chromatographie gazeuse / spectromètre de masse

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