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Hydrogen isotope ratios as a Larix detector in archaeological wood samples

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ABSTRACT

Identifying wood species in archaeological specimens is important for the evaluation of timber structures and the conservation of historic buildings. Microscopic wood anatomy is the most commonly used technique for species identification. However, its application is problematic for the analysis of deteriorated wood. In addition, a particular challenge is the distinction of Picea from Larix due to their similar microscopic features.

Recently, an analysis of stable isotopes of cellulose has shown that Larix is characterized by significantly more depleted deuterium values compared to Picea as well as other conifers from the Alpine region. To verify if this fact can be used in archaeological studies, we obtained 36 specimens, most of which were not clearly identified as larch or spruce. The cellulose could be extracted from 20 of them. We identified Larix and non-Larix species (Picea) without ambiguity from the deuterium content, except for one sample with an intermediate value. In conclusion, the evaluation of deuterium content is a valuable tool for the study of archaeologic wood.

1. Introduction

Archaeological wood is defined as deadwood used, modified, and eventually discarded by humans. The condition of this wood can vary between well preserved and highly deteriorated. Age alone is not crucial for deterioration, more important are factors such as the type of wood and the conservation environment (Florian, 1990). Different species usually have different wood morphological patterns, i.e., macroscopic as well as microscopic features (Schoch et al., 2004), and the identification of these patterns with microscopic wood anatomy analysis permits the recognition of the tree species. The clarity of surface information is essential for microscopic wood anatomy determination. However, the preservation status of the sample can make species identification difficult or even impossible (High and Penkman, 2020).

Knowing the sample species is important for understanding the properties and is a starting point in evaluating the timber structures. Identifying the wood species is also important for conserving historic building heritage (Machado et al., 2019) because different wood species may have different chemical compositions (Nilsson and Rowell, 2012).

A well-known limitation of microscopic wood anatomy technique is the difficulty in distinguishing between the genera Picea and Larix (Schoch et al., 2004), the so-called Picea-Larix problem (Bartholin, 1979). Nowadays, the high-resolution wood anatomical tools make it possible to distinguish between the two genera in well-preserved samples and in fresh wood (Anagnost, Meyer, and de Zeeuw, 1994). Still, archaeological wood is often too deteriorated, and these features cannot be observed (Mooney, 2016). Therefore, in many archaeological works, species identification remains unresolved. For example, some samples were called with a hybrid name as *Picea* sp./*Larix* sp., leaving the sample type unknown. Furthermore, different species can have different geographical origins and backgrounds, e.g., Gudmundsdottir (2013) stated "Pine and spruce can both be by human imported or driftwood, larches are always driftwood". In works on Roman subfossil wood and charcoal, it was unclear for 11% of the samples if they belonged to Picea or Larix (Moser et al., 2018). In this case, distinguishing the species was important to understand the sample's origin, being Picea present in the northern Apennines, whereas Larix is present only in the Alps (Pignatti, 1982).

In another work, it was also impossible to distinguish between the genera Larix and Picea in 16 archaeological samples (Malmros, 1990). The same difficulty was reported in works dealing with wood from Iceland, Svalbard, and Canada (Häggblom, 1982; Mooney, 2018, 2016; Steelandt et al., 2015) or the Swiss Alps (Oberhänsli et al., 2019; Reitmaier-Naef et al., 2020).

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The isotope analysis previously performed in the Bern laboratory showed that Larix is strongly deuterium depleted compared to all other conifer species. At the same time, no difference was found between, for example, the pine species *Pinus cembra* L. and a Picea tree (Arosio et al., 2020). To verify the suitability of deuterium analysis for identifying species in the context of archaeological and historical studies. We obtained 32 archaeological samples from various sites in the Swiss and Austrian Alps. In the Alps, the genera Picea and Larix are each represented in nature by only one species, *Picea abies* L. (spruce) and *Larix decidua* Mill. (larch).

Of these selected specimens, the species of 7 samples had already been determined by wood anatomical analyses, while in the others, the identification of larch or spruce was uncertain or not possible (type *Picea/Larix*). They were analyzed for their cellulose isotope ratios.

2. Methods

The samples originate mainly from different archaeological (e.g. Pichler et al., 2013; Reitmaier-Naef et al., 2020) and historical sites and settings in the Canton of Grisons (Switzerland) and the Tyrol (Austria). Exceptions are a subfossil root from the Tennen Mountains (Austria) as well as subfossil logs from Lej San Murezzan (Switzerland).

The samples consisted of small and large wood specimens ranging from milligrams to grams; some were particularly hard to cut, and others were fragile and broke in powder while handling. The samples were treated to extract cellulose as before (Ziehmer et al., 2018), however, the cellulose extraction was complicated for some samples and failed in a few cases since the wood remained unchanged even after cellulose extraction. Other samples vanished during the extractions. Moreover, some samples were highly slippery at cutting, possibly some carbonization happened. Thus, unfortunately, many samples were lost, and only 20 of the 36 specimens were fully analyzed. Its δD, $\delta^{18}O$, and $\delta^{13}C$ content were analyzed twice as in (Arosio et al., 2020). A list of samples with isotope measurements and assignment of species is given in Table 1.

3. Results and discussion

Species identification is based on specific δD values, which were shown to be strongly negative in Larix. We used the δD value threshold of −100‰ derived from the EACC dataset (Nicolussi et al., 2009; Ziehmer et al., 2018; Arosio et al., 2020) since all the samples were native of the Alpine region. Moreover, in a previous study on several species of Larix sampled in the botanical garden of the City Bern, we did not obtain results with values higher than −85‰; despite the water source in the Bern area is enriched in deuterium due to the lower altitude compared to tree line sites (Arosio et al., 2020). Fig. 1 and Table 1 show that δD analysis confirmed the species of all six samples already determined by wood anatomy, except for sample “smca-35″, which had a δD value of −58‰, a value that is above the Larix threshold. This finding stimulated a second wood anatomy analysis that indicated the sample as non-Larix genus, confirming the δD result. Thus, the deuterium analysis correctly identified the samples with uncertain or indefinite species assignmentif they belonged to Larix. Only one sample, GR11 with a δD value of −92‰ was above the Larix threshold and the assignment remains uncertain. This value is not an anomaly since, as there are several trees of the two species with δD values between −100‰ and −85‰ in the alpine conifer database (Fig. 2). The overlap between the two species decreases when the regions are analyzed separately (Fig. 3a). All samples come from tree trunks or branches, except the sample “TG-root” that originates from a root. The interpretation of its isotopic values is complex because the root production has specific phenological phases that may have isotopic effects (Ogée et al., 2009). Very few studies have been done on isotopes and particularly δD of roots (Yakir, 1992).

Altogether, these results show that δD is a robust marker of Larix species when values are below −100‰, even though the absolute value

Table 1
Codes, description and dD values of all the analyzed samples. Question marks indicate uncertain identification by wood anatomical (WA) analysis. If both species are listed (WA), the former is assumed to be more likely on the basis of wood anatomical characteristics. Samples from which it was not possible to extract cellulose have been omitted.

Sample code	Sample origin and description	Species WA	Species δD	agreement between δD and WA analysis	δD ‰ VSMOW
GR3	GR/St. Moritz, Lej San Murezzan	Larch/ Spruce	Larix	(yes)	−113.4
GR4	GR/St. Moritz, Lej San Murezzan	Larch ?	Larix	Yes	−126.5
GR5	GR/Surses, Mulegns, Val Faller-Plaz	Larch ?	Larix	Yes	−104.7
GR7	GR/Chur, Haldenstein, Maiensäss Fontanullia (GVG-Nr. 6–161)	Larch/ Spruce	Larix	(Yes)	−117.5
GR8	GR/Rhäzüns, Katholische Kirche Sogn Gieri	Larch ?	Larix	Yes	−124.7
GR9	GR/S-chanf, Bügl Suot 91	Spruce ?	Larix	No	−134.6
GR10	GR/Chur, Reichsgasse 15/ Kirche St. Regula	Larch ?	Larix	Yes	−134.8
GR11	GR/Chur, Kasernenstrasse 138 (Altes Zollhaus)	Larch ?	uncertain	Yes	−92.4
GR12	GR/Chur, Kasernenstrasse 138 (Altes Zollhaus)	Larch ?	non-Larix value	Yes	−69.2
GR13	GR/Chur, Kasernenstrasse 138 (Altes Zollhaus)	Conifere	non-Larix value	–	−72.6
GR14	GR/Surses, Marmorera, Cotschens, trough	Spruce/ Larch	non-Larix value	(yes)	−67.6
TG-root	Salzburg, Tennen Mountains	Spruce ?	non-Larix value ?	–	−83.6
bbui-1	Tyrol, mining site Mauk A, ore processing site	Spruce	non-Larix value	Yes	−66.8
smca-35	Salzburg Museum, mining timber	Larch	non-Larix value	No	−58.3
ksz-7	Tyrol, mining area Kogelmoos, Sagzeche, mining timber	Larch	Larix	Yes	−113.6
ksz-31	Tyrol, mining area Kogelmoos, Sagzeche, mining timber	Spruce	non-Larix value	Yes	−70.9
mosr-2	Tyrol, mining area Moosschrofen, construction timber	Larch	Larix	Yes	−130.2
mosr-5	Tyrol, mining area Moosschrofen, construction timber	Larch	Larix	Yes	−114.5
mosr-6	Abbaugrube Moosschrofen, Bühne	Larch	Larix	Yes	−112.4
mosr-17	Abbaugrube, Moosschrofen	Spruce/ Larch	Larix	–	−119.9

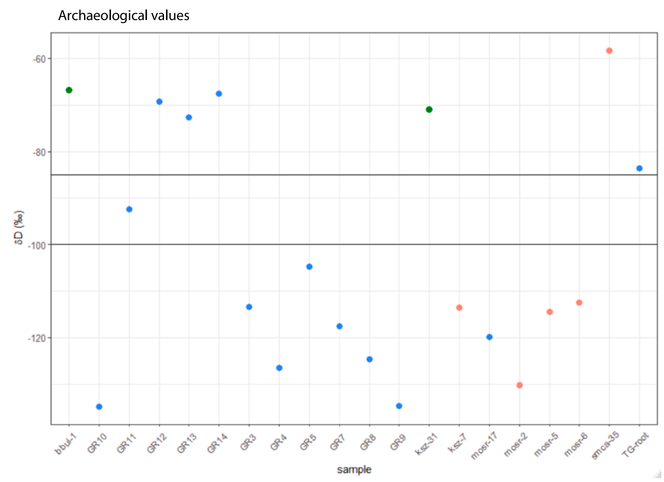

Fig. 1. Values of δD measurements in ‰ of the 20 archaeological samples. Sample codes as shown in Table 1. Colors according to the preceding wood anatomical determination: red: larch, green: spruce, blue: uncertain or indeterminate on the species level. The archaeological samples are separated into three groups. Twelve samples have a value below −100‰ and belong to the Larix species, seven have values above −80 ‰ are non-Larix, and one sample has a value between −100 and −85 ‰, and its assignment is uncertain. In the EACC, the threshold line is between −90/−100‰, with some local differences (Fig. 2).

of cellulose δD is influenced by the source water, which differs in different regions and can lead to value variability (Fig. 3a). Our data also show that the cellulose content does not affect the δD values of samples

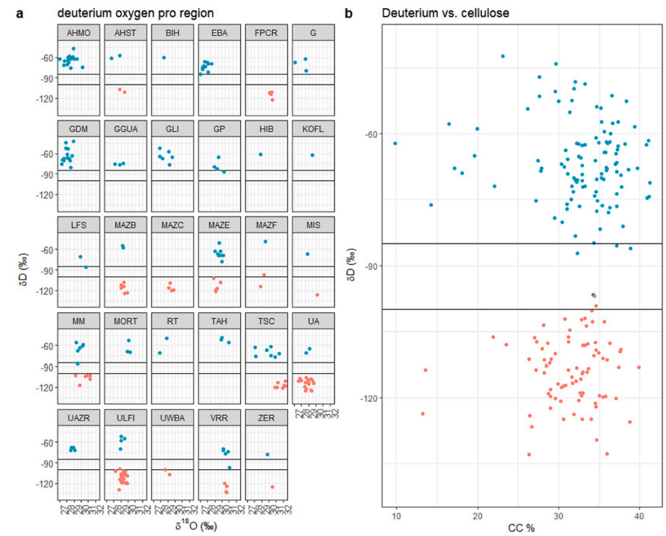

Fig. 3. Mean tree values of alpine conifer isotope record. Larch (in red) and cembran pine (in green). Panel a: Deuterium vs. oxygen values from different sites. Panel B: All deuterium values vs. cellulose content.

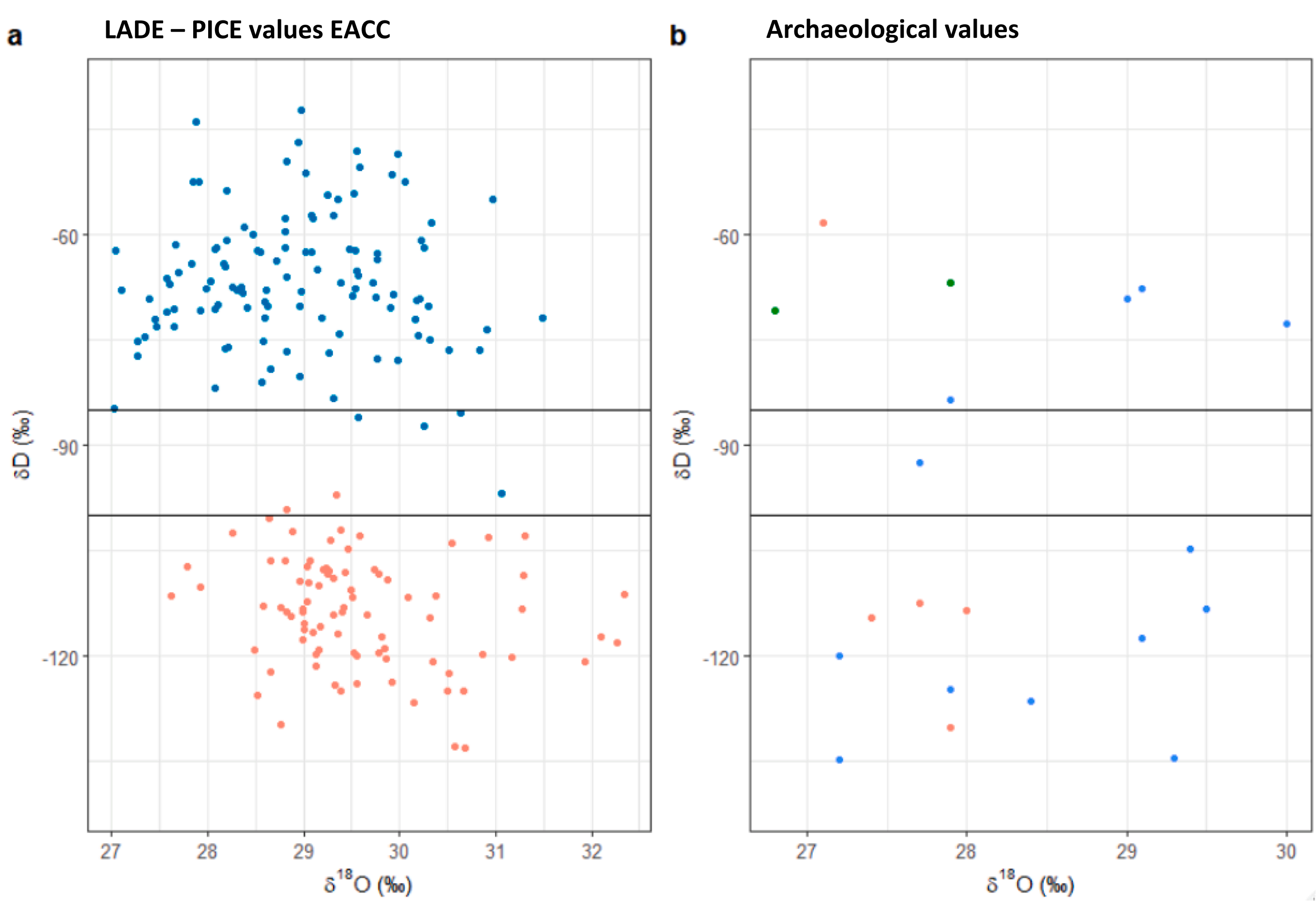

Fig. 2. Comparison between water isotopes of Eastern Alpine Conifer Chronology (EACC) and those of the archaeological samples. Panel a: δD and $\delta^{18}O$ mean values (‰) for each tree, larch (in red) and cembran pine (in green) from the EACC isotope database. Panel b: δD and $\delta^{18}O$ values (‰) of the archaeological samples, colors according to the preceding wood anatomical determination: red: larch, green: spruce, blue: uncertain or indeterminate on the species level (as in Fig. 1).

(Fig. 3b), indicating that δD analysis can provide reliable data for species identification with degraded samples when some cellulose can be extracted.

In conclusion, δD analysis identified all Larix specimens in the 20 poorly preserved archaeological samples. The reassignment of species was supported by new microscopic analysis where possible. Thus, the δD- analysis can be considered as an additional indication of the wood anatomical analysis, which is problematic when the sample is very degraded or has a very young cambial age.

These first results suggest that δD analysis contributes to studying archaeological wood samples and solving the Picea-Larix identification problem. However, this work was only carried out on a limited number of samples, all from the Alpine region. The robustness of the method should be verified by analyzing a more significant number of samples from areas outside the Alps, where meteoric water δD values may be very different. Our data also show that the state of preservation of archaeological wood can be problematic. As we found in some samples, complete fossilization or decay of wood decay makes cellulose extraction impossible.

Author contributions

TA performed the stable isotope analyses, TA drafted the first version of the manuscript. KN and MO collected the samples and made the cross dating. ML contributed to the evaluation of the results. ML, KN, and MO conceived of the presented idea. All authors provided comments to improve the manuscript.

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CRediT authorship contribution statement

Tito Arosio: Methodology, Data curation, Investigation, Visualization, Writing – original draft, Writing – review & editing. **Kurt Nicolussi:** Conceptualization, Resources, Writing – review & editing. **Monika Oberhänsli:** Writing – review & editing, Resources. **Markus Leuenberger:** Conceptualization, Methodology, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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