Stable (carbon, oxygen and hydrogen) isotopic analysis of a Roman wooden figurine

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Background

A sample of wood was provided for stable (carbon, oxygen and hydrogen) isotope analysis with a view to obtaining information on its chemical composition that may be useful for future geographic provenancing. Wood provenancing using stable isotopes is a developing field, but it was decided to take samples for analysis in anticipation of the future method development and before the wood is subjected to chemical preservation. This summary report describes sample preparation and analysis and reports the initial findings.

Method

The wood sample, believed to be oak was requested for analysis as a small radial lath with the intention of preserving the individual ring structure. This would permit dissection of early- and late-wood fractions of the tree ring as well as providing a measure of inter-annual variability that could further inform variability and uncertainty.

When measuring stable isotopes for palaeoclimatology or precision dating in ring porous species, the latewood only is analysed isotopically (Loader et al. 2020, McCarroll and Loader 2004). This is because the latewood isotope ratios relate most closely to the isotopic composition of the source water, carbon dioxide and the environmental conditions at the time of growth (wood formation). Early-wood has been shown to contain a proportion of photosynthate from previous years and may also record additional isotopic fractionation due to physiological processes (Hill et al. 1995).

In this case unfortunately, the material provided was very soft and degraded. This meant that it was neither possible to identify individual rings nor to sub-divide early- and late-wood fractions. As the sample could only be processed to cellulose as a bulk sample of early- and late-wood from multiple rings, this could impact upon the resulting isotope value its utility for provenancing in the future.

The sample wood was waterlogged and showed signs of degradation (softening and discoloration). The sample was divided into three sub-samples for preparation of cellulose. The first two sub-samples comprising degraded wood in the form of identifiable woody fragments, the third, represented the remainder of the sample and considered of lower quality.

The three sub-samples were processed to alpha-cellulose using methods modified from Loader et al. 1997. After treatment some of the cellulose exhibited orange flecks. Upon closer investigation it was considered that these could represent some form of resistant iron staining (not removed during chemical processing) or more likely fungal strands bound between the cellulose fibres. Fortunately, it was possible to manually remove any significant orange flecks from the two primary sub-samples under magnification. The cleaned cellulose was homogenised and then freeze dried. The third sub-sample proved more difficult to clean in this way and retained some contamination.

Samples of 0.3-0.35mg of cellulose were weighed into silver foil capsules for isotopic analysis of carbon and oxygen isotopes. Samples were pyrolised over glassy carbon at 1400°C using a Flash HT elemental analyser interfaced with a Delta V isotope ratio mass spectrometer. Oxygen and carbon

isotopes were expressed using the delta notation (Coplen 1995). Analytical precision determined on standard cellulose is typically better than 0.1 and 0.3 per mille (Loader 2013, 2019).

Approximately 30% of the hydrogen is cellulose is exchangeable with environmental waters, and so it is necessary to derivitise or equilibrate cellulose prior to hydrogen isotope determination. Hydrogen isotopes were measured by Dr Marco Lehmann at the University of Bern, Switzerland using a triple isotope method (after Filot et al 2006, Loader et al. 2015). Hydrogen isotope ratios determined by mass spectrometry on the equilibrated cellulose thermally degraded to H_2 gas at 1420°C.

Results

Isotopic analysis of the wood sub-samples are presented in Table 1. Data for sub-sample 1 and 2 are presented. Sub-sample 3, which represented the remainder of the sample material, and although presented for here completeness, was not considered to have been cleaned adequately and we recommend that these values are considered for exclusion from future provenancing tests.

	CARBON : $\delta^{13}C$	OXYGEN : $\delta^{18}O$	HYDROGEN : $\delta^{2}H_{(non\text{-}exchangeable)}$
	(per mille VPDB)	(per mille VPDB)	(per mille VSMOW)
Sample 1	-23.41	28.64	-52.50
Sample 2	-23.52	28.68	-51.36
Sample 3	*-24.22*	*27.95*	*-67.70*
Mean (1&2)	**-23.46**	**28.66**	**-51.93**

Summary

The above data provide an insight into the C,H,O isotopic composition of the Roman wooden figurine. Additional analyses may be performed in future to refine these data and to further explore the natural variability of stable (C,O,H) isotopes across the European distribution of oak.

At present is it not possible to conclusively or reliably provenance the sample using the stable isotope data alone as there is currently an absence of high-quality C,H,O isotopic data for Europe with which to complete a detailed and quantitative provenancing study. There are many uncertainties relating to the use of modern isotopic data for provenancing which must also be considered and addressed in future work. In part these uncertainties relate to changes in the isotopic signal both spatially and temporally (Treydte et al. 2007). Work has been initiated to develop a modern provenancing dataset using tree ring stable isotopes.

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