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Sensitivity of whole wood stable carbon and oxygen isotope values to milling procedures

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RATIONALE: Milling of wood samples is a widely applied preparation method for pooling tree-rings from different trees or periods of several years for determination of $\delta^{13}C$ and $\delta^{18}O$ values. In this study, whole wood samples were milled using different procedures in order to evaluate potential effects of this preparation method on $\delta^{13}C$ and $\delta^{18}O$ values.
METHODS: Subsamples of a 5 cm^3 wood piece of a single tree-ring from a lowland white fir were used. The samples were milled with different setups: (i) two and three stainless-steel balls, (ii) 3, 5 and 8 min milling time, and (iii) discontinuous and continuous milling. The $\delta^{13}C$ values were measured using an elemental analyser connected to an IsoPrime mass spectrometer and $\delta^{18}O$ values using a Thermo Scientific MAT 253 mass spectrometer and a TC/EA connected by a ConFlo IV.
RESULTS: The results show that varying the milling procedure does not alter the $\delta^{13}C$ and $\delta^{18}O$ values in comparison to non-milled blank samples. For shorter milling times, an increased variance of $\delta^{18}O$ values is recorded, probably caused by isotopic gradient between early- and latewood portions of the tree-ring and thereby biasing the insufficiently homogenised samples. No overheating effects on the $\delta^{13}C$ and $\delta^{18}O$ values were detected.
CONCLUSIONS: Milling of wood samples for carbon and oxygen isotope analyses is an appropriate preparation method.

During the last decade, an increasing number of studies have employed carbon and oxygen stable isotope ratios from tree-rings as climate proxies.[1–4] Many of these studies use ball or centrifugal mills to pulverise and homogenise the wood samples.[1,5,6] The application of these mills is particularly useful if larger sample amounts are processed. This is, for instance, the case if material of the same calendar year from several trees is pooled[1,7,8] or if material of multiple years is analysed as a single sample.[9,10]

We use this common wood preparation procedure for $\delta^{13}C$ and $\delta^{18}O$ analyses in our laboratory, and observed a warming of the wood samples during milling and a burning smell. Pure cellulose (Merck Chemicals, Darmstadt, Germany) that was continuously milled for 8 min exhibited 1.4‰ more negative $\delta^{18}O$ values than non-milled cellulose. This may be explained by oxidation of the cellulose with atmospheric oxygen, which has an approximately 4‰ more negative $\delta^{18}O$ value (23.5‰[11]) than cellulose ($\delta^{18}O = 27.5$‰), and may thus result in a lower $\delta^{18}O$ value. The oxidation is triggered by the heat caused by the mechanical energy produced during the milling procedure. This change in $\delta^{18}O$ values was not, however, observed after 8 min of continuous milling with a cryogenic mill. The heat may also have an influence on the $\delta^{13}C$ values of the whole wood. Resin will be the first component of the wood sample to be converted into CO_2 as a result of being heated.[12] Due to the resin having a lower $\delta^{13}C$ value than the other wood components,[13] the released CO_2 will be enriched in ^{12}C. This would lead to higher $\delta^{13}C$ values for the milled whole wood samples.

These observations question the applicability of milling as a preparation method for isotopic analyses. Our working hypothesis is that the milling procedure leads to a warming of whole wood samples, resulting in decreased $\delta^{18}O$ values due to oxidation with atmospheric oxygen and an increase in $\delta^{13}C$ values due to CO_2 losses. In order to verify this hypothesis, we performed a systematic test using a homogeneous wood sample.

We tested if different milling procedures (number of stainless-steel balls, milling duration and continuity of the milling process) altered the $\delta^{13}C$ and $\delta^{18}O$ values of whole wood samples. Longer milling duration might lead to an increased development of heat and alteration of the $\delta^{13}C$ and $\delta^{18}O$ values. A larger number of stainless-steel balls might result in a larger release of friction heat. Finally, discontinuous milling might lead to interim cooling of the samples and prevent or reduce alteration effects. The results of this test could be of interest to the community using milling for tree-ring sample preparation.

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