This is the published version of a paper presented at EGU General Assembly 2018, Vienna, Austria, April 8-13, 2018.

Citation for the original published paper:
Tree-ring cellulose exhibits several interannual $^{13}$C signals on the intramolecular level
In: Geophysical Research Abstracts, EGU2018-17509-2

N.B. When citing this work, cite the original published paper.

Permanent link to this version:
http://urn.kb.se/resolve?urn=urn:nbn:se:umu:diva-145982
Tree-ring cellulose exhibits several interannual $^{13}$C signals on the intramolecular level

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Measurements of carbon isotope contents ($^{13}$C/$^{12}$C, $\delta^{13}$C) in tree rings provide retrospective information about the short and long-term dynamics of plant ecophysiological, and paleo-environmental traits. They are commonly based on $^{13}$C/$^{12}$C ratios of cellulose, and interpreted with respect to fractionation related to CO$_2$ diffusion into plants and its fixation by Rubisco (diffusion-Rubisco - DR - fractionation). However, primary metabolites such as glucose are known to exhibit intramolecular $^{13}$C/$^{12}$C differences of the order of 10$^\circ$ which reflect $^{13}$C fractionation by enzyme reactions downstream of Rubisco (Post-Rubisco - PR - fractionation).

PR fractionation is not commonly considered in dendrochronological studies. It has not yet been investigated whether glucose monomers of cellulose show intramolecular $^{13}$C differences. Furthermore, it is unknown whether PR fractionation varies among years, and whether DR and PR fractionations introduce distinct $^{13}$C/$^{12}$C signals. To test this, we isolated the glucose monomers of Pinus nigra tree rings, and determined $^{13}$C/$^{12}$C ratios of all intramolecular glucose carbon positions by quantitative $^{13}$C NMR. The resulting dataset consists of 6 time series of positional $^{13}$C/$^{12}$C ratios with annual resolution, extending from 1961 to 1995.

Tree-ring glucose exhibits intramolecular $^{13}$C/$^{12}$C differences of the order of 10$^\circ$. Cluster analysis revealed several independent intramolecular $^{13}$C signals. These signals constitute distinct channels of information about both the DR interface and associated environmental triggers, as well as PR processes related to downstream C allocation. Thus, analysis of intramolecular $^{13}$C signals can extract more information with better quality from tree rings. This might enhance our understanding of biogeochemical, ecophysiological and paleo-environmental phenomena.