



Tree-ring cellulose exhibits several interannual ^{13}C signals on the intramolecular level

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Measurements of carbon isotope contents ($^{13}\text{C}/^{12}\text{C}$, $\delta^{13}\text{C}$) 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 $^{13}\text{C}/^{12}\text{C}$ 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 $^{13}\text{C}/^{12}\text{C}$ differences of the order of 10‰ 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 $^{13}\text{C}/^{12}\text{C}$ signals. To test this, we isolated the glucose monomers of *Pinus nigra* tree rings, and determined $^{13}\text{C}/^{12}\text{C}$ ratios of all intramolecular glucose carbon positions by quantitative ^{13}C NMR. The resulting dataset consists of 6 time series of positional $^{13}\text{C}/^{12}\text{C}$ ratios with annual resolution, extending from 1961 to 1995.

Tree-ring glucose exhibits intramolecular $^{13}\text{C}/^{12}\text{C}$ differences of the order of 10‰. 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.