

Evaluation of the age related systematic patterns of stable oxygen and carbon isotope values of Swiss stone pine (Pinus cembra L.) Eastern Carpathians, Romania

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Tree-ring derived stable isotope time series are becoming increasingly important parameters in investigation of past environmental changes. However, potential age related trend-bias on these parameters, and the proper handling of it, is still not well understood. We here present measurements on a new multicentennial data set of annually resolved stable oxygen (δ 18O) and carbon (δ 13C) isotope compositions from 3 living and 4 subfossil Stone pine (Pinus cembra) samples collected at a timberline habitat in the Eastern Carpathians (Romania) to evaluate any potential systematic ontogenetic pattern on their δ 18O and δ 13C data. Oldest analyzed ring represented 129th, 135th and 142th cambial year in the living and 115th, 130th, 165th and 250th cambial year in the subfossil samples. The fact that Stone pine samples are backbone of the longest dendrochronological series both in the Alps and the Carpathians arouses special interest concerning their potential in stable isotope dendroclimatological research. Whole-ring samples were prepared to alpha-cellulose by the modified Jayme-Wise method. Cellulose samples were analyzed by a high-temperature pyrolysis system (Thermo Quest TC-EA) coupled to an isotope ratio mass spectrometer (Thermo Finningan Delta V). A ring by ring (i.e. non-pooled) approach was followed since age-related trends are by definition intrinsic to individual tree-ring series so pooling of rings may distort the detection of the trends. Raw measured δ 13C values have been corrected for changes in the atmospheric CO₂ regarding both its stable isotope signature and mixing ratio.

Neither isotopic parameter showed any age related variance bias suggesting a homoscedastic character. Alignment of the δ 13C data by cambial age revealed a relatively short period (~40 years) of systematic behaviour manifested in a ~1‰ enrichment in 13C over a <40 year-long period after germination. While a moderate but persistent positive trend (~0.33‰ per 100years, p<10-10) can be observed for carbon discrimination afterwards. In contrast, hardly any systematic juvenile pattern or any long-term trend could be detected for δ 18O data.

Based on the 80 year-long common ontogenetic period (from the 35th to the 115th ontogenetic year) we found a very narrow range of offset $\sim 1 \%$ both for $\delta 180$ (from 28.32% to 29.31% and for $\delta 13C$ (from -23.07% to -22.14% between individual trees over the past 500 years. Despite the very coherent level found for the studied stone pine individuals scaling of the overlapping records is a highly recommended pre-processing step in future isotope chronology construction.

The short juvenile-effect of $\delta 13C$ record can be eliminated if <40 yr periods are omitted from the records. As an alternative approach, preliminary tests suggest that subtraction of a best-fit logarithmic trend might help to retain the juvenile rings into the final $\delta 13C$ chronology to improve the replication over time. However, our preliminary results suggest that $\delta 180$ from Stone pine cellulose can be used without detrending to build isotope chronologies therefore the potential to preserve the low-frequency variability in the parameter is excellent.

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