Supplement of

Radiocarbon dating of alpine ice cores with the dissolved organic carbon (DOC) fraction

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Estimation of the carbonate removal efficiency for WIOC samples

To test if incomplete removal of carbonates can potentially explain the $F^{14}C$ DOC-WIOC offset observed in our dataset, we estimated the carbonate removal efficiency of our procedure. We applied the following model, based on isotopic mass balance:

$$F^{14}C_{\mathrm{WIOC}} = \frac{m_{\mathrm{meas}} * F^{14}C_{\mathrm{meas}} - m_{\mathrm{res.carb}} * F^{14}C_{\mathrm{carb}}}{m_{\mathrm{meas}} - m_{\mathrm{res.carb}}}, \quad (1)$$

where $F^{14}C_{\mathrm{WIOC}}$ denotes the true value of the sampled WIOC, m_{meas} and $F^{14}C_{\mathrm{meas}}$ the measured carbon mass and $F^{14}C$, $m_{\mathrm{res.carb}}$ and $F^{14}C_{\mathrm{carb}}$ the mass and $F^{14}C$ of residual carbonate carbon on the filter (assuming an average value of 0.1 corresponding to an age of ~20 ka; Amundson et al., 1994). With

$$m_{\mathrm{res.carb}} = c_{Ca^{2+}} * 0.3 * 0.5 * m_{ice} * (1 - x_{eff}), \quad (2)$$

where $c_{Ca^{2+}}$ is the mean Ca^{2+} concentration in the analyzed samples, 0.3 the ratio of the atomic weights of carbon (12 amu) and Ca (40 amu), 0.5 the assumed fraction of airborne Ca associated with carbonate (Meszaros, 1966), m_{ice} the ice sample mass. The WIOC carbonate removal efficiency, x_{eff}, was assumed to be the same for all our samples from the four different sites. x_{eff} was finally derived in a least square approach by minimizing the difference between

$F^{14}C$-DOC and $F^{14}C_{WIOC}$. Due to the lack of carbonate concentration data, Ca^{2+} concentrations are here used as a tracer of calcium carbonate instead (or if also not measured, the available, most representative data for the respective glacier; see main manuscript Table 3). Calcium carbonate is the most common geological form, occurring e.g. as calcite ($CaCO_3$), aragonite ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$.

The so derived estimate of an average removal efficiency of ~96 % would amount to an average residual carbonate carbon amount on the WIOC filter of ~4 μgC (see main manuscript Table 3). We tested this value for its robustness. By selecting different values for the two critical parameters $F^{14}C_{carb}$ and the assumed fraction of airborne Ca associated with carbonate, e.g. 0.05 (corresponding to an age of ~30 ka) and 0.8, respectively, the resulting average removal efficiency varies by only +1 %. If allowing x_{eff} to vary dependent on the sampling site, a nearly perfect match between $F^{14}C$ DOC-WIOC can be achieved for all samples including Chongce (average x_{eff} = 95 % with a 4 % variability, the average residual carbonate carbon amount is slightly lower in this case, amounting to 3±1.5 μgC). With this model set-up, the highest removal efficiency is estimated for the samples from the Belukha ice core with 99%.

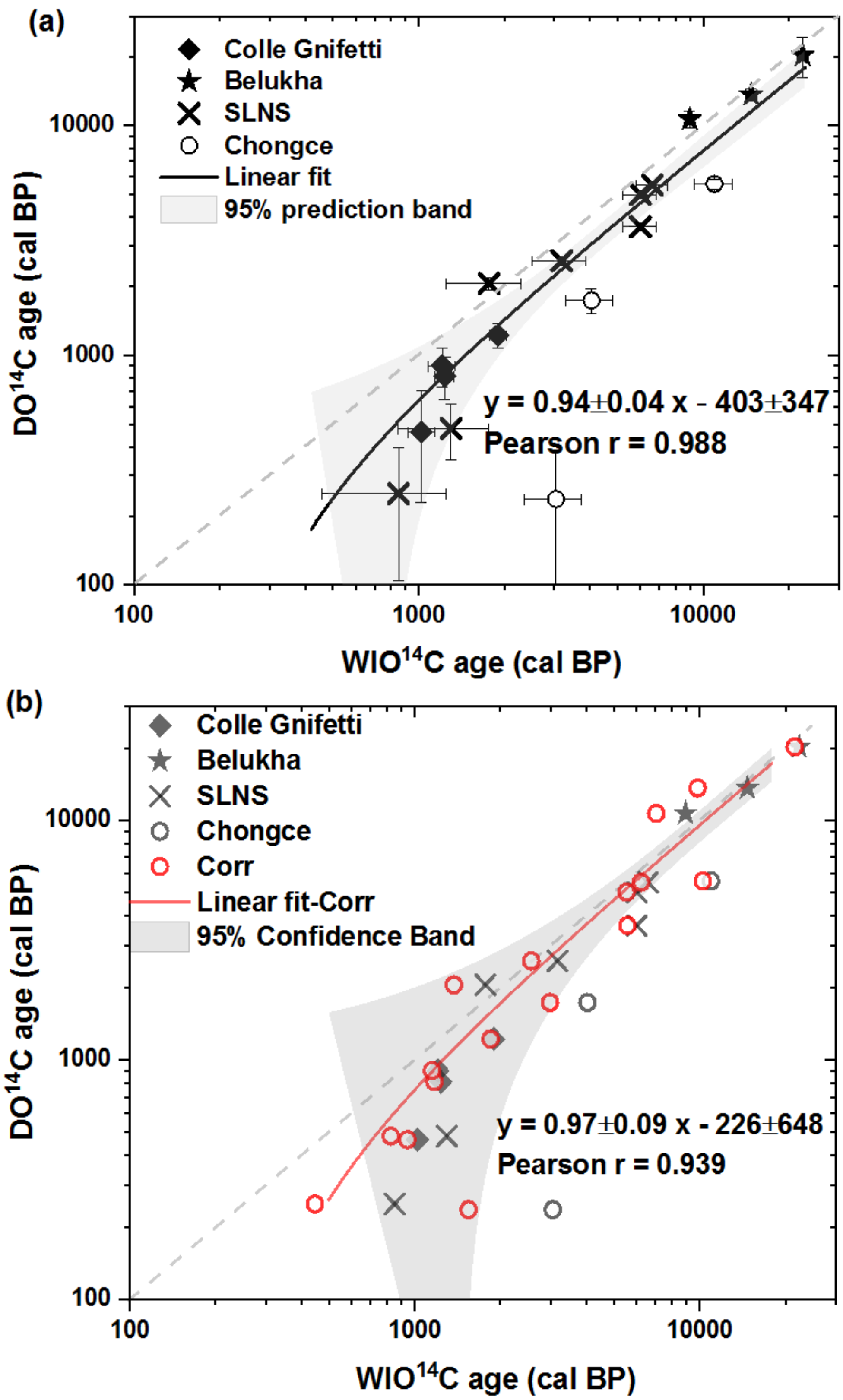

Figure S1. Comparison between calibrated ^{14}C ages of the DOC and WIOC fractions in (a) and after accounting for the effect of residual carbonates to WIO^{14}C ages (b). For the linear fits shown, the original data from Chongce (open symbols) is excluded in (a) but is included when carbonate contribution was accounted for in (b).

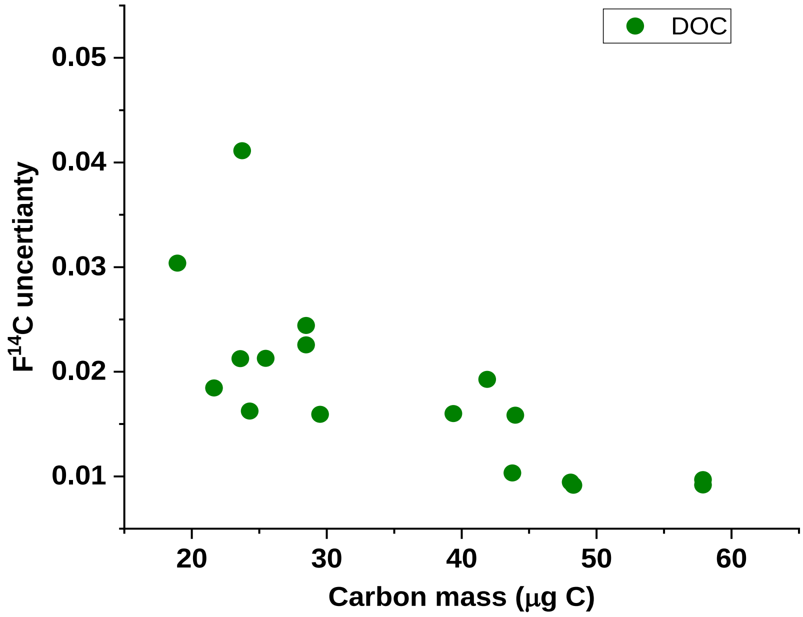

Figure S2 Analytical $F^{14}C$ 1σ uncertainty for DOC versus sample carbon mass.

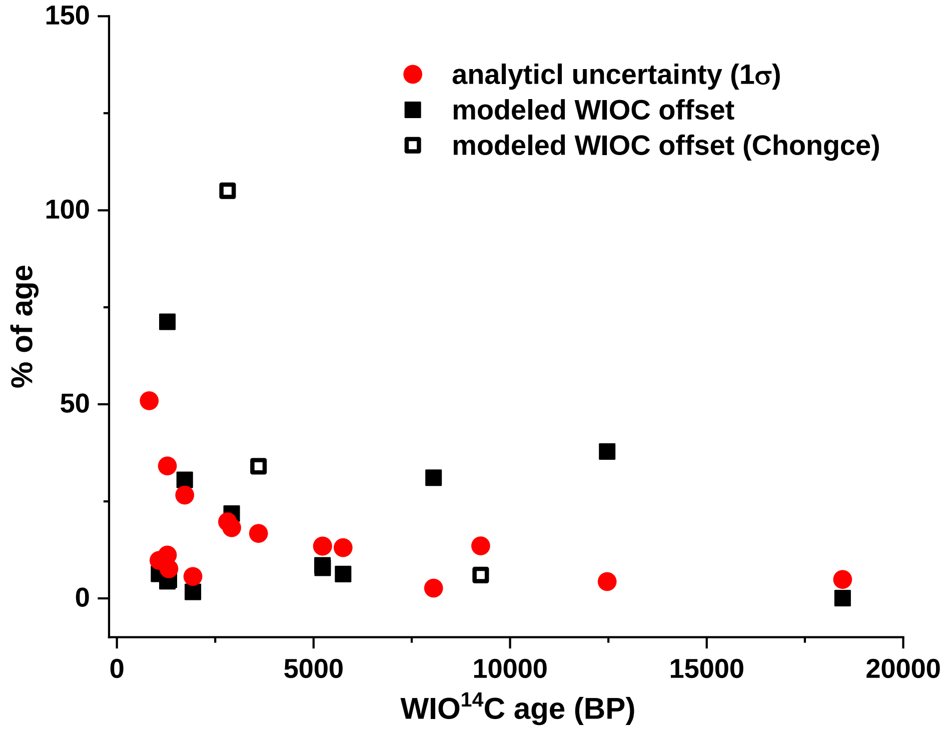

Figure S3 Modeled ^{14}C age offset in the WIOC fraction associated with contribution from residual carbonate carbon (squares; open squares for Chongce) and the $WIO^{14}C$ dating uncertainty (1σ, red dots) for each sample as percentage of the respective age versus the $WIO^{14}C$ age.

References

Amundson, R., Wang, Y., Chadwick, O., Trumbore, S., McFadden, L., McDonald, E., Wells, S. and DeNiro, M., Factors and processes governing the ^{14}C content of carbonate in desert soils. Earth and Planetary Science Letters, 125, 385-405, 1994.

Meszaros E., On the origin and composition of atmospheric calcium compounds, Tellus, 18:2-3, 262-265, DOI: 10.3402/tellusa.v18i2-3.9627, 1966.