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

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Estimation of in-situ produced ^{14}C incorporated into DOC

The absolute number of in-situ produced ^{14}C atoms per gram ice can be calculated following Lal et al. (1987):

$$C_{in-situ} = \frac{P_o}{\frac{\rho A}{\Lambda} - \lambda} \times \left(e^{-\frac{\lambda z}{A}} - e^{-\frac{\rho z}{\Lambda}}\right) \quad (1)$$

Where $C_{in\text{-}situ}$ is the number of produced ^{14}C atoms per gram ice. P_o is the in-situ ^{14}C production rate (atoms g^{-1} ice yr^{-1}) which depends on altitude and latitude (Table S1) and was estimated from Lal (1992), see numbers in Table 4 (main manuscript). ρ, A and z are the ice density in kg L^{-1}, accumulation rate in m w.e. yr^{-1} and depth in m w.e., respectively. λ is the radiocarbon decay constant. Λ is the adsorption mean free path length in g cm^{-2}, given as 150 g cm^{-2} in Lal and Jull (1990). No annual net accumulation rates for the new cores from Colle Gnifetti, Belukha, and Chongce are available yet. Therefore, we here relied on previously reported values for ice cores extracted very close-by (Colle Gnifetti from Jenk et al., 2009; Belukha from Henderson et al., 2006; and Chongce from Hou et al., 2018). For the SLNS core, the annual net accumulation rate was roughly estimated by a glaciological flow model (2p-model; Bolzan, 1985; Uglietti et al., 2016) fitted to the $DO^{14}C$ dated horizons (0.21 m w.e. yr^{-1}). The annual net accumulation rates are summarized in Table S1.

Of the total number of in-situ produced ^{14}C atoms per gram ice, Hoffmann (2016) found a fraction of 11-25 % incorporated into the DOC fraction when performing a neutron irradiation experiment on Alpine ice core samples. We here used a value of 18±7 % to finally calculate the resulting shift in $F^{14}C$-DOC (i.e. the in-situ ^{14}C production caused offset of $F^{14}C$-DOC). With the DOC concentration known (derived from sample ice mass and DOC carbon mass):

$$F^{14}C_{shift} \approx ((^{14}C \text{ atoms produced per g ice*sample ice mass*}f_{DOC})/(m_{DOC}/m_a * N_A))/(R) \quad (2)$$

where f_{DOC} is the fraction of in-situ ^{14}C incorporated into DOC, m_{DOC} the DOC carbon mass of the sample, m_a the atomic mass of C, N_A the Avogadro constant and R the $^{14}C/^{12}C$ ratio of the modern standard at the time of AMS analysis. From Eq. 2 it becomes obvious, that the effect of in-situ ^{14}C on DOC-$F^{14}C$ is smaller the higher the DOC concentration in the ice. All input values and results are summarized in Table 4 (main manuscript).

Estimation of the carbonate removal efficiency for WIOC samples

To test if a reasonably high, but slightly incomplete removal of carbonates is sufficient for potentially explaining the $F^{14}C$ DOC-WIOC offset observed in our dataset, we estimated the carbonate removal efficiency of our procedure during WIOC sample preparation (main text, Sect. 2). We applied the following model, based on isotopic mass balance:

$$F^{14}C_{\mathrm{WIOC}} = \frac{m_{\mathrm{meas}} * F^{14}C_{\mathrm{meas}} - m_{\mathrm{res.carb}} * F^{14}C_{\mathrm{carb}}}{m_{\mathrm{meas}} - m_{\mathrm{res.carb}}}, \qquad (3)$$

where $F^{14}C_{\mathrm{WIOC}}$ denotes the true (initially unbiased) 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. $F^{14}C_{\mathrm{carb}}$ is derived for an assumed contemporary age of the deposited carbonate of 12.5 kyrs, with a wide range of ±7.5 kyrs to derive reasonable uncertainty estimates. (Amundson et al. (1994) reported an age for carbonates of ~20 kyrs but carbonates in loess deposits can be younger. Due to the lack of carbonate concentration data, we here relied instead on Ca^{2+} concentrations as a tracer of calcium carbonate, the most common geological form, occurring e.g. as calcite ($CaCO_3$), aragonite ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$.

With

$$m_{\mathrm{res.carb}} = c_{Ca^{2+}} * 0.3 * f_{carb} * m_{ice} * (1 - x_{eff}), \qquad (4)$$

where $c_{Ca^{2+}}$ is the Ca^{2+} concentration in the analyzed samples (see Table S2), 0.3 the ratio of the atomic weights of carbon (12 amu) and Ca (40 amu), f_{carb} the assumed fraction of airborne Ca associated with carbonate (considering a value of 0.5±0.2, Meszaros (1966)), m_{ice} the ice sample mass and x_{eff} the WIOC carbonate removal efficiency..

The best solution of x_{eff} was finally searched for by a least squares approach, minimizing the residual sum of squares of the offset between in-situ corrected $F^{14}C\text{-}DOC_i$ (see Table 4 of main manuscript) and $F^{14}C_{\mathrm{WIOC}_i}$ as calculated in Eq. 3 (i.e. minimizing the offset between in-situ ^{14}C corrected $F^{14}C$-DOC and $F^{14}C_{\mathrm{WIOC}}$). We did sets of model runs across the range of parameter values given above, and for a complete propagation of errors, also considered the range of uncertainty for the offset (composed of the analytical uncertainty and the uncertainty of the in-situ ^{14}C DOC correction). The carbonate removal efficiency x_{eff}, was either assumed to be similar for all four sites, yielding an average of 98±2 %, or allowed to vary for each site individually with the aim to derive a more complete assessment of the modeling uncertainty (Table S2). The later, because high likelihood for differences in source and transport of carbonates to the individual sites can be assumed (i.e. a high likelihood that in reality, the values of parameters $F^{14}C_{\mathrm{carb}}$ and f_{carb} vary from site-to-site).

Despite all the uncertainties involved, implying that an accurate correction is not feasible, this modeling approach clearly demonstrates that a carbonate removal procedure, incomplete by only a few percent, is sufficient to explain an offset between $F^{14}C$ DOC-WIOC of the size we observed (Figure 5 in the main manuscript). The offset is close to the analytical uncertainty (Figure S2). Consistent with discussions in previous studies, we thus consider this effect to be a very likely explanation.

Table S1 Metadata for the study sites.

Site (year drilled)	**Coordinates and elevation**	**Location**	**Ice core length (m)**	**Accumulation rate (m w.e. yr^{-1})**	**References**
Colle Gnifetti (2015)	45°55’45.7’’N, 7°52’30.5’’E 4450 m asl.	Western Alps, Swiss-Italian border	76	0.45*	Jenk et al. 2009; Sigl et al., 2018
Belukha (2018)	49°48'27.7"N, 86°34'46.5"E 4055 m asl.	Altai Mountains, Russia	160	0.5&	Henderson et al., 2006; Uglietti et al., 2016
SLNS (2010)	38°42'19.35"N, 97°15'59.70"E 5337 m asl.	Shule Nanshan Mountains, China	81	0.21#	Hou et al., submitted
Chongce (2013, core 1)	35°14'5.77"N, 81°7'15.34"E 6010 m asl.	Kunlun Mountains, China	134	0.14+	Hou et al., 2018

*Previously reported value for a core collected from the same drilling site in 2003 (16 m distance).
&Previously reported value for a core collected from the same location in 2001 (90 m distance).
#Estimate based on a glaciological flow model (2p model) and $DO^{14}C$ dated horizons.
+Previously reported value for Chongce core 3, extracted less than 2 km away from the same glacier plateau.

Table S2 Estimated carbonate removal efficiency for WIOC samples and residual carbonate carbon on the analyzed WIOC filters. Ca^{2+} concentrations, used here as a tracer for carbonates, are average values for the sampled ice core sections (or site if data not available).

Core section	Ca^{2+} concentration (ppb)	ice sample mass (kg)	removal efficiency (%)	residual carbonate C (μgC)	average removal efficiency (%)	$F^{14}C$-WIOC after accounting for residual carbonate [&]	WIOC Cal age after accounting for residual carbonate (cal BP) [&]
CG110	100	0.570	70-100	0.0-2.0	98±2	0.878±0.012	974±123
CG111	110	0.539				0.851±0.011	1199±104
CG112	61	0.536				0.855±0.015	1169±142
CG113	59	0.549				0.787±0.011	1872±138
Belukha412	4191	0.443	99-100	0.0-0.2		0.410±0.028	8114±588
Belukha414	7566	0.336				0.261±0.040	12945±1805
Belukha415	3737	0.319				0.106±0.012	21881±1085
SLNS101	1400*	0.420	97-100	0.0-3.0		0.929±0.055	686±415
SLNS113	same	0.427				0.875±0.053	1111±485
SLNS122	same	0.424				0.824±0.050	1602±530
SLNS127	same	0.483				0.714±0.051	2918±714
SLNS136	same	0.374				0.532±0.047	5840±846
SLNS139	same	0.485				0.533±0.047	5814±848
SLNS141-142	same	0.413				0.498±0.047	6460±846
CC237	2170[#]	0.352	93-97	2.5-6.5		0.752±0.074	2561±962
CC244	same	0.311				0.668±0.058	3648±892
CC252	same	0.174				0.324±0.050	10742±1667

* Ca^{2+} concentrations are not available for SLNS, instead the average Ca^{2+} concentration over the last 7000 years measured on the nearby Puruogangri ice cap on the central Tibetan Plateau are used here(Thompson et al., 2006).

[#] Ca^{2+} concentration over the period of 1903-1992 from another core drilled on the Chongce ice cap by a different group (Chongyi et al., 2016).

[&] Calculated using the average removal efficiency of 98±2 %.

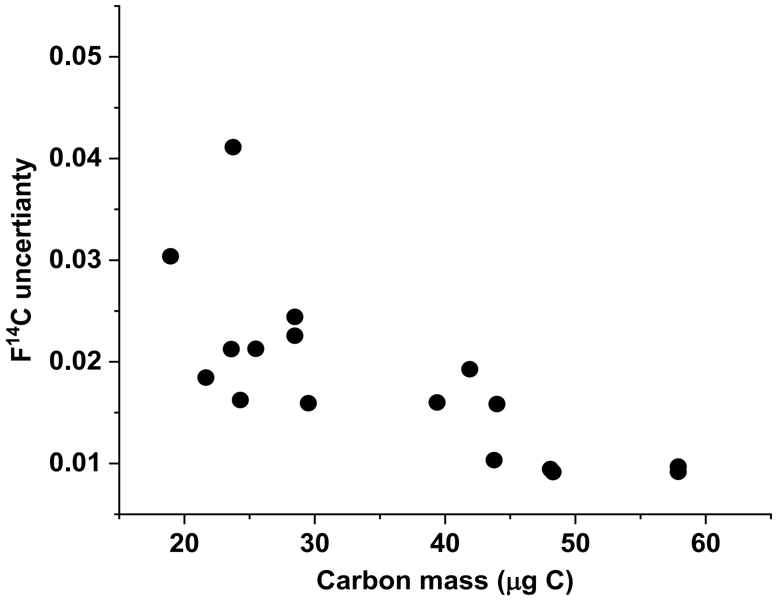

Figure S1 Analytical $F^{14}C$-DOC 1σ uncertainty versus sample DOC carbon mass.

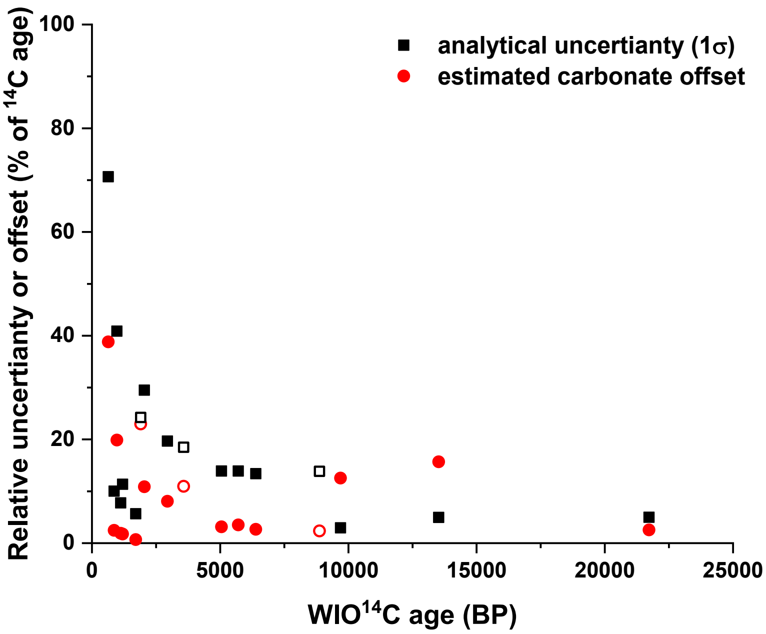

Figure S2 Relative size of analytical uncertainty and carbonate related offset (assuming 98 % carbonate removal efficiency) for ^{14}C dating using the WIOC fraction. Plotted for each sample against its measured WIOC ^{14}C age. Samples with visibly high loading of mineral dust from the Chongce ice core are highlighted by open symbols.

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