

Radiocarbon dating of alpine ice cores

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An accurate chronology of alpine ice cores is essential to interpret the climate-signal and atmospheric-pollution history archived in glaciers. The radiocarbon in water-insoluble organic carbon (WIOC) has emerged as a valuable tool for dating alpine ice cores.

The challenge of alpine ice-core dating

The most common ice-core dating approach is annual layer counting, which relies on seasonal variations in chemical and physical signals, such as ammonium, stable isotope ratios ($\delta^{18}\text{O}$, $\delta^2\text{H}$) and solid electrical conductivity. However, pronounced thinning beyond a certain depth limits this approach in its application for ice cores.

To establish a complete age-depth scale down to the bedrock, simplified ice-flow models can be employed (e.g. Dansgaard and Johnsen 1969), but they are unable to resolve small-scale variations in ice flow (i.e. thinning/strain), particularly closer to the bedrock, where the often complex glacier geometries of high-mountain glaciers become increasingly important. Also, they rely on fundamental assumptions, such as constant accumulation, that likely do not reflect the actual conditions over time. Even complex 3D models cannot convincingly simulate the age of the deepest sections, if no additional age constraints are available (e.g. Licciulli et al. 2020).

Absolute time horizons can pin down the age of the ice. A valuable marker for alpine ice cores is the signal from atmospheric nuclear-weapon testing, showing up as a clear peak in 1963 CE in multiple proxies, such as tritium or cesium-137. Known volcanic eruptions, such as Katmai in 1912 CE and Tambora in 1815 CE, indicated by peaks in sulfate and conductivity, are also commonly used as time markers (Herren et al. 2013). Moreover, Saharan dust events during the 20th century (e.g. 1977, 1947 and 1901 CE) are well documented and can easily be identified in the European Alps (often visually, coinciding with peaks in calcium concentration in the ice cores). However, these events were only documented for the last two centuries, and these horizons cannot be established in deeper sections where no conventional dating techniques are applicable.

The development of radiocarbon analysis of WIOC

Radioactive nuclides entrapped in the ice offer an opportunity to obtain absolute dates. The environmental radionuclide ^{210}Pb , with a short half-life of 22.3 years, enables the dating of ice over roughly one to two centuries (Gäggeler et al. 2020). The noble gas ^{39}Ar and ^{32}Si with a half-life of 268 ± 8 years and of 144 ± 11 years, respectively, have been demonstrated as ideal dating isotopes for ice samples from the last thousand years

(Morgenstern et al. 2010; Ritterbusch et al. 2022).

The recent developments in atom-trap trace analysis (ATTA) have allowed scientists to substantially reduce the required amount of ice to 1–3 kg for ^{39}Ar dating (Ritterbusch et

al. 2022). The long-lived ^{81}Kr , with a half-life of 229,000 years, can date ice up to 1.5 million years old (Tian et al. 2019). However, due to the low abundance of ^{81}Kr , ~10 kg of Antarctic ice or 20–40 kg of ice from the Tibetan Plateau is recommended for sampling (Tian et al. 2019). Given the half-life of

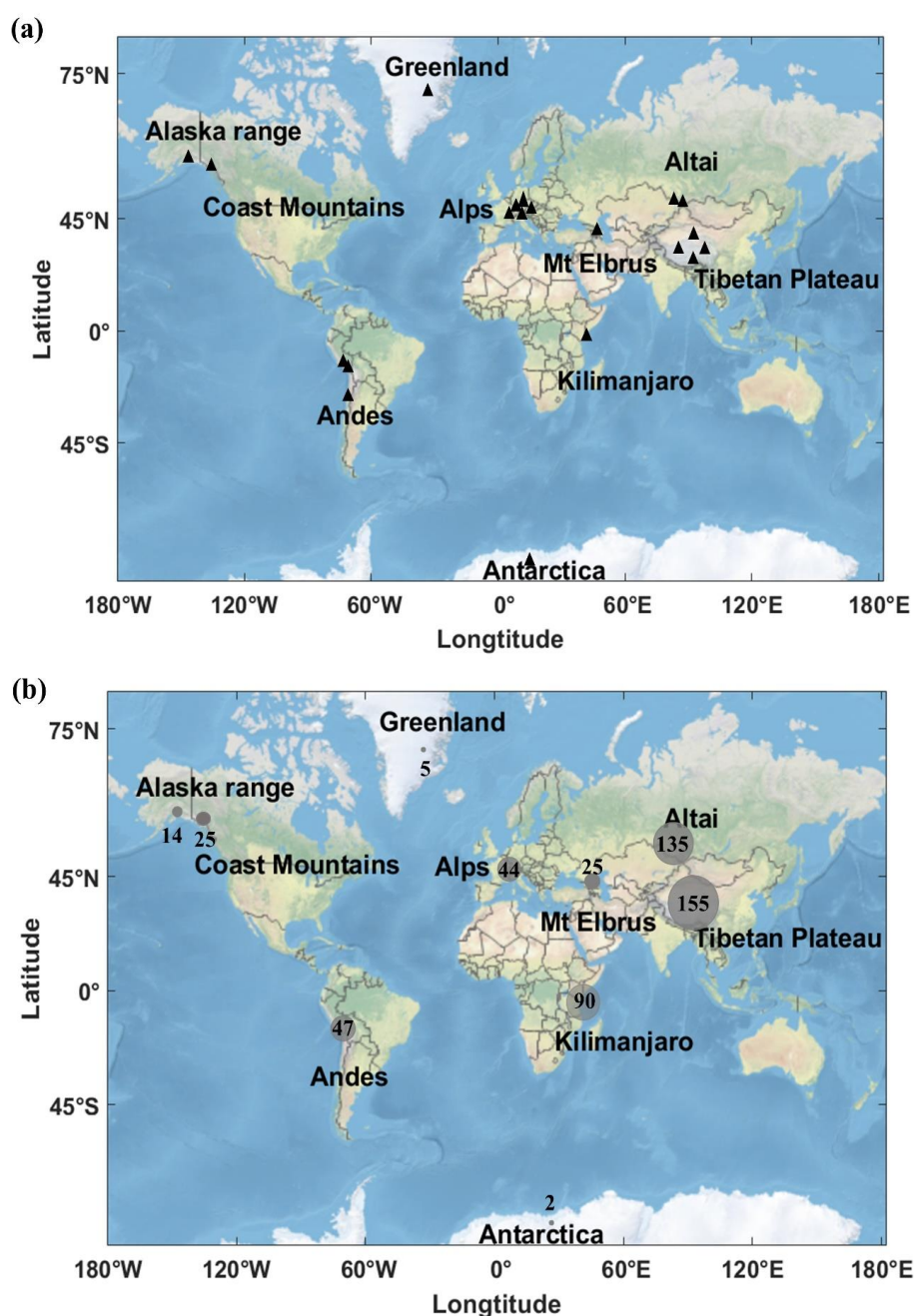


Figure 1: Map showing (A) the sites from which ice samples were ^{14}C dated with WIOC; and (B) the averaged WIOC concentrations ($\mu\text{g}/\text{kg}$) for different regions. The size of the gray circles on the map corresponds to the WIOC concentrations.

5370 years, radiocarbon (^{14}C) is considered the most suitable radionuclide for dating ice samples up to around 20,000 years old, covering most of the time range typically accessible by alpine ice cores (Uglieri et al. 2016).

Previously, ^{14}C dating of ice was only possible where sufficient organic matter such as plant, wood or insect fragments was found (Thompson et al. 1998). However, the occurrence of such findings is rare in glacier ice, and even when they are present, do not allow for continuous dating. To overcome this challenge, Jenk et al. (2009) introduced the use of water insoluble organic carbon (WIOC) for ^{14}C dating of alpine ice cores and Uglieri et al. (2016) later validated the method.

Carbonaceous particles are a major component of the atmospheric aerosol and deposit onto the glacier by precipitation. They are composed of two main bulk fractions: organic carbon (OC) and elemental carbon (EC). OC can be split into WIOC and dissolved organic carbon (DOC; see below) by solubility. WIOC and EC are separated based on their specific thermal properties (combustion temperatures). The micro-carbon ^{14}C dating method relies on the finding that WIOC originated solely from biosphere emissions prior to the use of fossil fuels (~1850 CE; Jenk et al. 2006). Once emitted, the ^{14}C decays according to its half-life time, starting the radiometric clock. A detailed method description for WIOC ^{14}C -dating can be found in Uglieri et al. (2016).

Various ice samples have been dated using micro- ^{14}C WIOC since the introduction of this technique (Figs. 1–2). WIOC concentrations ranged from 2–15 $\mu\text{g}/\text{kg}$ in samples from the Polar Regions to 155 $\mu\text{g}/\text{kg}$ in ice from the Tibetan Plateau (Fang et al. 2021; Uglieri et al. 2016), while Alpine ice samples used for dating contained $44 \pm 14 \mu\text{g}/\text{kg}$ on average (Fang et al. 2021; Uglieri et al. 2016; Fig. 1). To date, the oldest sample was determined with an age of ~22 kyr BP at the bottom of an ice core retrieved from Belukha (Russian Altai; Fig. 2). On Colle Gnifetti (CG03 core) in the European Alps, the oldest ice retrieved from the Alps was >15 kyr BP, and on Illimani in the Andes ~12.6 kyr BP (Fang et al. 2021; Jenk et al. 2009; Sigl et al. 2009; Uglieri et al. 2016; Fig. 2).

The majority of dated alpine ice cores, however, was younger than 10 kyr BP (e.g. Uglieri et al. 2016). The dating precision strongly depends on the ^{14}C content of the sample, defined by the carbon mass and the age of the sample, i.e. its $^{14}\text{C}/^{12}\text{C}$ ratio. The uncertainty decreases sharply with increased carbon mass due to the blank correction. Therefore, a total carbon amount of 10 μg , typically equivalent to around 300–500 g of ice, is recommended for reliable dating.

The most recent developments and outlook

In glacier ice, the higher concentration of DOC compared to WIOC (by a

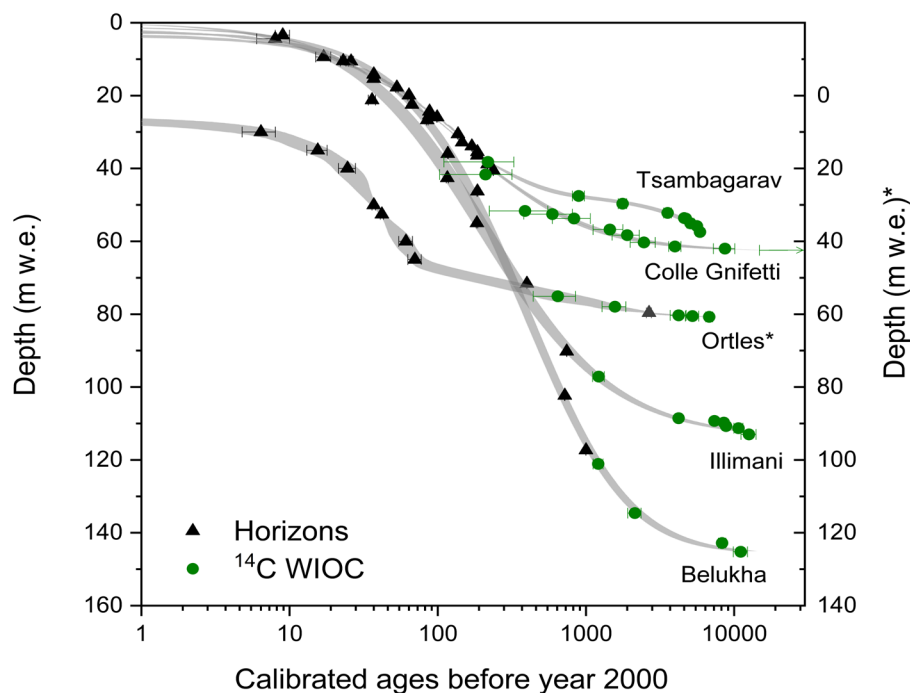


Figure 2: Ice-core chronology based on ^{14}C dating (modified from Figure 6 in Uglieri et al. 2016). Horizons and ^{14}C results are shown as black triangles and green circles, respectively. Gray shaded areas represent the 1 σ range of the respective fit for retrieving a continuous age–depth relationship. To enhance visibility, the curve for the Mt Ortles glacier was shifted downward by 20 m water equivalent (m w.e.) and is referenced in the right-hand y axis, denoted with an asterisk (*).

factor ranging from 2 to 5; Fang et al. 2021) provides a motivation to investigate the possibility of using DOC for ^{14}C dating. The required mass of ice could potentially be further reduced, if WIOC and DOC were to be extracted from the same piece of ice. Two studies found that the DOC fraction can be biased in its $^{14}\text{C}/^{12}\text{C}$ ratio due to in situ ^{14}C production by cosmogenic radiation (Fang et al. 2021; May 2009). This limits the theoretically achievable gain in dating precision given by the higher carbon mass.

Nevertheless, Fang et al. (2021) showed the great potential of the DOC fraction to date ice from sites where in situ ^{14}C production is relatively low. This is the case for sites at altitudes of 4000–5000 masl and below (low radiation), and/or characterized by snow accumulation rates greater than 0.5–1 m water equivalent (less exposure) such as in the European Alps. Method details can be found in Fang et al. (2019), also describing the most recent setup allowing simultaneous extraction of DOC and WIOC samples for ^{14}C dating of ice, which was built at the Laboratory for Environmental Chemistry (PSI, Switzerland).

In conclusion, due to lower demands of ice mass and the time coverage of the lowest and oldest ice-core sections, ^{14}C analysis has become a crucial and widely applied tool for the dating of ice cores from mountain glaciers. Although the possibility of using the DOC fraction for ice-core dating has been demonstrated, further studies are needed to explore the full dating potential in terms of ice requirement and analytical precision, and accuracy for using both OC fractions, extracted from the same sample.

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