



Soil depth gradients of organic carbon-13 – A review on drivers and processes

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Abstract

Background and aims Soil organic carbon (SOC) dynamics are vital in the context of climate change and sustainable soil management. The $\delta^{13}\text{C}$ signatures of SOC are powerful indicators and tracers of C fluxes through soils and of transformation processes within soils. Depth gradients of $\delta^{13}\text{C}$ can be considered as their archive. However, many different drivers and processes impact $\delta^{13}\text{C}$ signatures of SOC simultaneously, thus hampering their interpretation.

Methods Here we summarize the current knowledge about drivers, processes and C sources determining the $\delta^{13}\text{C}$ signatures of organic matter along soil profiles.

Results The largest $\delta^{13}\text{C}$ gradients within soil profiles ($>10\%$) have been observed at sites where vegetation has shifted between C3 and C4 plants, thus changing the isotopic signatures of C inputs. In soil profiles without such vegetation changes, the $\delta^{13}\text{C}$ signatures typically increase by 1–3‰ from topsoil to subsoil. Three main reasons for this are (i) the decreasing $\delta^{13}\text{C}$ of atmospheric CO_2 (Suess effect) has led to a depletion in plant biomass by about 2.0‰ since 1850, (ii) increasing atmospheric CO_2 concentrations have also depleted plant biomass by about 1.8‰, and (iii) isotopic fractionation occurs during continuous microbial C recycling and necromass accumulation. Moreover, a greater mobility of ^{13}C -enriched hydrophilic dissolved organic C and other C input sources may impact $\delta^{13}\text{C}$ gradients in soils.

Conclusions External drivers, such as climatic and atmospheric changes, affect the $\delta^{13}\text{C}$ signature of C inputs, and have stronger and increasing influence on $\delta^{13}\text{C}$ gradients in soil profiles compared to soil internal processes.

Keywords Carbon cycle · ^{13}C · Fractionation · Microbial necromass · Suess effect · Photosynthetic pathway

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Introduction

Terrestrial carbon (C) pools and the underlying processes affecting their dynamics are important in the

context of climate change mitigation, because ecosystems can act as both, sources and sinks of C. The future climate and functioning of ecosystems will be affected by the stability of the terrestrial carbon sink of which approximately 2270 Pg C is stored as soil organic carbon (SOC) in the upper two metres of the world's soils (Jackson et al. 2017). This is equivalent to 200 years of current anthropogenic emissions (11 Pg C yr⁻¹ 2010–2019) (Friedlingstein et al. 2020; Mathieu et al. 2015). Isotopic analysis and approaches can elucidate the exchange of carbon between the pedosphere and the atmosphere (Metya et al. 2021), as well as the geosphere (Kalks et al. 2021), biosphere (Iversen et al. 2012) and hydrosphere (Hindshaw et al. 2016). In natural materials the abundance of the stable isotope ¹³C is between 0.96% and 1.16% of the C atoms, while the radioactive isotope ¹⁴C contributes < 10⁻¹² % and the rest is ¹²C (Meija et al. 2016). The abundances of stable isotopes can be expressed by the $\delta^{13}\text{C}$ annotation as the difference (in per mille, ‰) between the isotopic ratio (of heavy and light isotopes) of a sample and the isotopic ratio of a reference standard (e.g. for C Pee Dee Belemnite). The $\delta^{13}\text{C}$ signature of C compounds is useful for tracing and quantifying recent C fluxes and pools, and can elucidate the origin and environmental conditions during the formation of the compounds up to a few thousand years ago (Boutton 1996; Ehleringer et al. 2000). Soil depth gradients in $\delta^{13}\text{C}$ of SOC evolve as a result of internal and

external drivers and processes, which are related to the soil C turnover, pedogenesis and the climate (Staddon 2004; Briones et al. 1999; Stevenson et al. 2005). $\delta^{13}\text{C}$ depth gradients can elucidate palaeoecological developments and can help analysing mechanisms resulting in C storage changes (Krull and Retallack 2000; Diochon and Kellman 2008). The $\delta^{13}\text{C}$ signature of SOC typically rises by 1–3‰ with depth in most soil profiles around the world (Fig. 1) (Wynn et al. 2005; Högberg et al. 2005; Boström et al. 2007; Ehleringer et al. 2000; Torn et al. 2002; Balesdent et al. 2018b; Dalal et al. 2005; Roscoe et al. 2001).

There are several hypotheses that attempt to explain this phenomenon: (i) the influence of atmospheric or ecosphere changes, (ii) the preferential decomposition of different C components, (iii) the isotopic fractionation during the degradation of SOC, continuous necromass recycling and the distribution of fungal and bacterial biomass within soil profiles, (iv) the CO₂ fixation and methane metabolism of microorganisms, (v) the input of root-derived C to the soil and (vi) the transport of dissolved organic carbon (DOC) (Boström et al. 2007; Ehleringer et al. 2000; Högberg et al. 2005; Nel and Cramer 2019; Bird et al. 2003; Kohl et al. 2015; Ni et al. 2020). Importantly, these drivers are not mutually exclusive and a number of them can simultaneously impact the $\delta^{13}\text{C}$ signature, which makes it difficult to quantify their impact

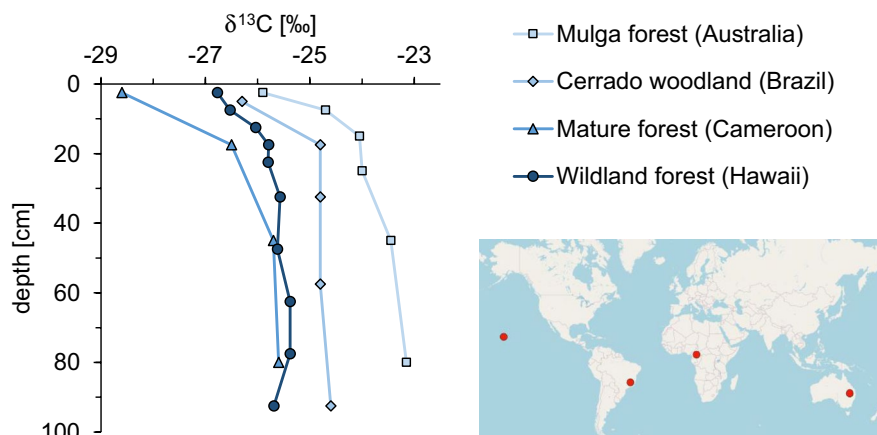


Fig. 1 Typical patterns of the $\delta^{13}\text{C}$ signature of SOC within soil profiles at sites with stable native vegetation and different climatic conditions. Mulga forest (Australia; 516 mm precipitation) (Dalal et al. 2005), Cerrado savannah woodland (Brazil; 1340 mm) (Roscoe et al. 2001), mature forest (Cameroon;

1560 mm) (Guillet et al. 2001) and wildland forest (Hawaii; 3000–4600 mm) (Bashkin and Binkley 1998). Reference is made here to the database of (Balesdent et al. 2018b) as a collection of soil $\delta^{13}\text{C}$ depth gradients

separately. Furthermore, the processes determining the inputs, development and isotopic fractionation of deep (> 30 cm soil depth) soil C have not been fully explored, despite that on average 47% of the SOC of the uppermost metre is stored at a depth of 30–100 cm (Mathieu et al. 2015; Ehleringer et al. 2000; Balesdent et al. 2018a). The slow turnover rates in the subsoil due to low microbial activity make it even more difficult to measure fractionation processes in situ (Mathieu et al. 2015). Even in the topsoil, measurement accuracy and the implementation of the gas sampling limits the detection of discriminations against ^{13}C of <0.5‰ during soil respiration processes (Boström et al. 2007). In soils with carbonates, these must be first removed without damaging the SOC. Otherwise soil inorganic C could overlay the depth gradient of the $\delta^{13}\text{C}$ signature of SOC (Torn et al. 2002). Often not all the factors influencing the $\delta^{13}\text{C}$ signature of SOC are known and considered, therefore interpretations of depth gradients are sometimes ambiguous. The following sections in this paper review the internal and external drivers, C sources and processes affecting the $\delta^{13}\text{C}$ signature of SOC, and compile them into an overall picture to provide a basis for the interpretations of isotopic depth gradients (Fig. 2).

External drivers and C sources affecting the $\delta^{13}\text{C}$ signatures of SOC

The isotopic signatures of C inputs to the pedosphere are affected by numerous external environmental

drivers influencing the previous photosynthetic C assimilation, and depend on the biological and geological sources of the C compounds. The following subchapters discuss the importance of atmospheric and other environmental drivers to the isotopic signatures of plant C assimilates and the subsequently formed soil organic C, as well as the impact of changing compositions of C sources, which are also affected by environmental conditions.

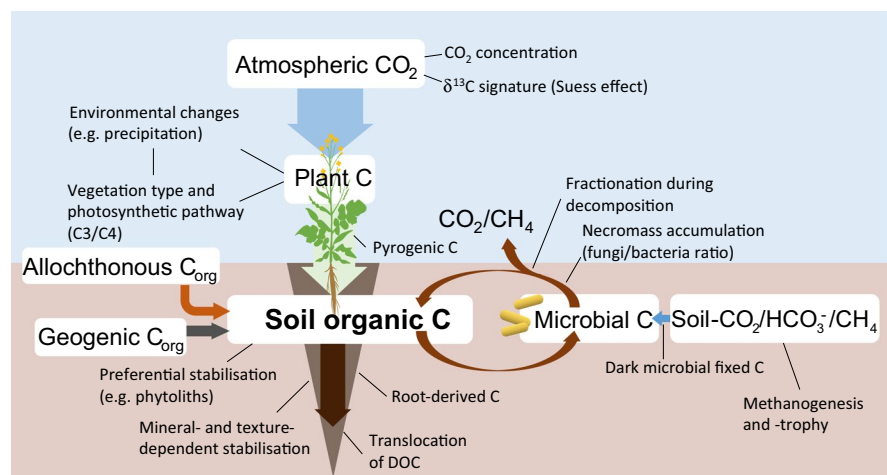
Drivers affecting the $\delta^{13}\text{C}$ signatures of plant-assimilated C

As plant biomass is the main source of SOC, factors controlling the fractionation of ^{13}C during photosynthesis influence the isotopic signature of SOC. During photosynthesis, plants discriminate against ^{13}C isotopes driven by the diffusion resistance of their stomata and photosynthetic enzymes, or rather by the reaction rates between CO_2 and Ribulose-1,5-bisphosphate carboxylase-oxygenase (RuBisCO) during carboxylation processes (Schweizer et al. 1999; Bowling et al. 2008). The isotopic difference of the produced plant tissue and the consumed CO_2 (isotopic discrimination) can be estimated for C3 plants using the following equation (Farquhar et al. 1989):

$$\Delta\delta^{13}\text{C}_p = a + (b - a)(p_i/p_a) \quad (1)$$

where the constants a and b represent the fractionation of ^{13}C during diffusion through the stomata and the net fractionation during carboxylation predominantly by RuBisCO, respectively. The variables p_i

Fig. 2 Internal and external drivers, carbon sources and processes affecting the $\delta^{13}\text{C}$ signature of soil organic carbon. White boxes represent the carbon pools related to the pedosphere and the arrows show the fluxes between these pools. Affiliated keywords describe the drivers, processes and sources of carbon that have the potential to affect the isotopic signatures of bulk soil organic carbon. Plant graphics designed by Julia Schröder



and p_a are the intracellular and ambient partial pressure of CO_2 respectively. The discrimination against ^{13}C during photosynthesis generally provokes more negative isotopic signatures of plant tissues and SOC than those of atmospheric CO_2 , but does not lead to depth gradients of the isotopic signature within soil profiles by itself when the $\delta^{13}\text{C}$ signature of plant C input to the soil are stable. Atmospheric drivers and changing environmental conditions over time, which modify the isotopic signature of photosynthetically assimilated C, can contribute to depth gradients of the $\delta^{13}\text{C}$ signature of SOC owing to the larger amount of newer material in the topsoil than in the subsoil (Fig. 3a) (Balesdent et al. 2018a). The transport of decomposed and transformed carbon compounds to the subsoil and the addition of fresh litter inputs to the topsoil let ^{14}C age gradients evolve. The mean age of SOC in global topsoils (0–30 cm) is around 1.4 kyr calculated by compiling global radiocarbon profiles, while the SOC in subsoils (30–100 cm) is on average 8.3 kyr old (Shi et al. 2020). Nevertheless, fresh carbon assimilates can have a visible impact on the $\delta^{13}\text{C}$ signatures of SOC, especially in the topsoil. For example, a decade of experimentally CO_2 -enriched atmospheric conditions with depleted isotopic signatures led to a significant increase of the depth gradient

of the $\delta^{13}\text{C}$ signature of SOC (Fig. 3b) (Iversen et al. 2012).

Changes in the $\delta^{13}\text{C}$ signatures of atmospheric CO_2

The $\delta^{13}\text{C}$ signature of the atmospheric CO_2 is about -8.7‰ today, which is 2.0‰ less than in 1850 before industrialisation (Fig. 4) (Rubino et al. 2019; Keeling et al. 2001). The decreasing $\delta^{13}\text{C}$ signature is caused by the combustion of isotopically depleted fossil fuels (so called Suess effect) and is transmitted through plants into the SOC (Graven et al. 2017; Högberg et al. 2005). The impact on $\delta^{13}\text{C}$ gradients in soils by the Suess effect depends on the soil type, the ratio of fresh C inputs to long-term stabilised C, the translocation of newly produced C into deeper soil layers, and the general C turnover time (cf. Fig. 3).

The $\delta^{13}\text{C}$ signature of the atmospheric CO_2 also changed in the Holocene before anthropogenic modifications, thus in the time period of pedogenesis of many soils. The CO_2 of the glacial atmosphere during the Last Glacial Maximum had a $\delta^{13}\text{C}$ of -7.1‰ , which rose to a mean value of -6.4‰ in the Holocene (Marino et al. 1992). During the Holocene, the $\delta^{13}\text{C}$ signature of atmospheric CO_2 increased by about 0.25‰ during the first 5 kyr before present (BP), and decreased by 0.05‰ after 6 kyr BP (before

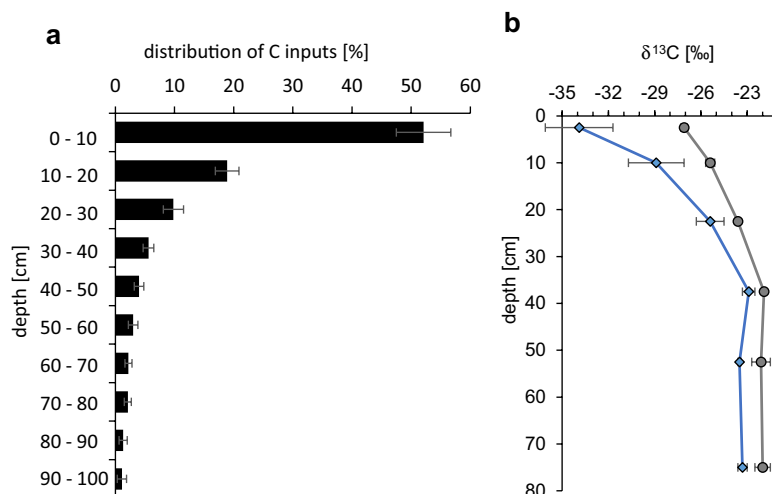


Fig. 3 **a** Global estimate of the distribution of the last 50 years of carbon inputs (1965–2015) within soil profiles. Data originate from (Balesdent et al. 2018a). **b** Depth gradient of the $\delta^{13}\text{C}$ signature of SOC under a sweetgum plantation with Free-Air Carbon dioxide Enrichment (FACE). The blue line shows

the depth gradient of $\delta^{13}\text{C}$ after the plants have been grown in an atmosphere with 565 ppm CO_2 and a depleted signature of $\delta^{13}\text{C} = -51\text{‰}$ for eleven years, and the grey line represents the reference soil without manipulation. Data adapted from (Iversen et al. 2012)

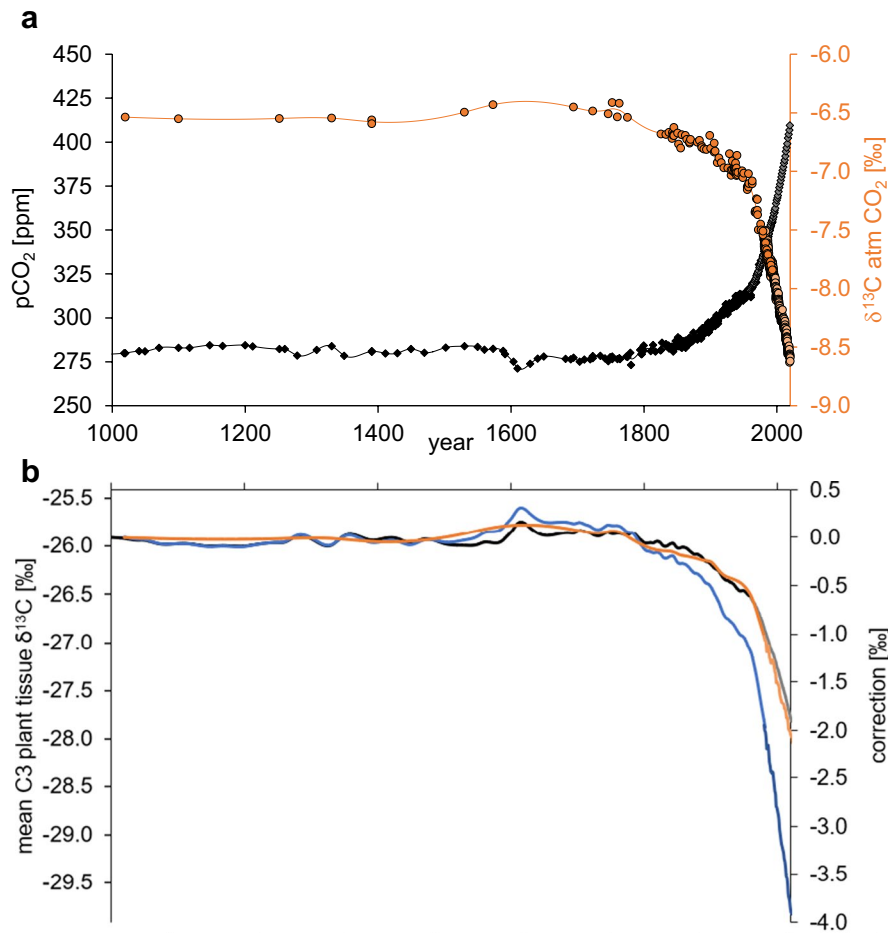


Fig. 4 **a** Atmospheric CO₂ concentration and δ¹³C signature from 1000–2022. Atmospheric CO₂ records since 1959 (grey diamonds) based on yearly averages of direct observations from Mauna Loa (Hawaii) and the South Pole by the Scripps Institution of Oceanography (SCRIPPS) (Keeling et al. 2001). Furthermore, average δ¹³C signatures since 1980 derived from monthly seasonally adjusted data based on flask air samples from Mauna Loa (orange dots). The older data of the atmospheric CO₂ concentration (black diamonds) and the δ¹³C signature (orange dots) originate from Law Dome ice core records generated by Rubino et al. (2019). **b** Correction factors for δ¹³C signatures and calculated δ¹³C signatures of mean C3 plant tissues produced during the last 2000 years related to increasing atmospheric CO₂ concentrations (pCO₂) (black/grey line), decreasing δ¹³C signatures (orange/rose line), and their combined effect (blue/dark blue line).

anthropogenic influence), driven by changes in the terrestrial biosphere and the marine carbonate cycle (Elsig et al. 2009). In particular, terrestrial biomass production and the uptake of isotopically light CO₂ by plants grew during the early Holocene, which

For the δ¹³C signatures since 1980, seasonally-adjusted values were chosen (Keeling et al. 2001). The net isotopic difference between the atmospheric CO₂ and the developed C3 plant tissue was approximated in relationship to changes in pCO₂ using an equation from Schubert and Jahren (2015): $\Delta\delta^{13}C = [28.26 * 0.22(pCO_2 + 23.9)] / [28.26 + 0.22(pCO_2 + 23.9)]$. The isotopic signature of plant tissues at different points in time was calculated by: $\delta^{13}C_p = [(R_a / (\Delta\delta^{13}C / 1000 + 1)) / R_{VPDB} - 1] * 1000$. R_a and R_{VPDB} are the isotopic ratios of the atmospheric CO₂ and the reference standard, respectively. For the correction only of changes of pCO₂ the δ¹³C signature of 1019 was converted into a constant R_a , while the changing δ¹³C signatures of atmospheric CO₂ were used for the combined effect (changing pCO₂ and δ¹³C). The correction value was always calculated by $\delta^{13}C_{p(t=x)} - \delta^{13}C_{p(t=0)}$

promoted an increasing atmospheric δ¹³C signature (Eggleston et al. 2016; Elsig et al. 2009). Most soils in the northern latitudes are younger than 12 kyr BP because ice advances have displaced older material and left periglacial deposits or bare bedrock material

(Mathieu et al. 2015). Isotopic signatures of SOC produced during initial soil development in the early Holocene (SOC older than 6 kyr) should be more depleted than the signatures of SOC of preindustrial times, and could act as a small driver against the generally increasing $\delta^{13}\text{C}$ signatures. However, the most pronounced changes in the isotopic signatures of plant assimilates have been observed recently due to the continuously increasing rate of anthropogenic CO_2 emissions.

Changes in the concentration of atmospheric CO_2

Atmospheric CO_2 concentration changes throughout the planet's history affects the isotopic signature of plants and therefore also SOC (Fig. 4) (Canadell et al. 2021; Graven et al. 2020; Farquhar 1991). The speed of the increase in atmospheric CO_2 concentration between 1900 and 2019 was at least ten times faster than at any other point of time in the last 800 kyr (Canadell et al. 2021). This is a unique driver of temporal changes in the isotopic signatures of C inputs into the pedosphere. Increasing atmospheric CO_2 concentrations (p_a) are accompanied by decreasing isotopic signatures of the plant tissues because the amount of active carboxylation sites on RuBisCO and the carboxylation efficiency are increased, so that a larger amount of CO_2 entering the leaves is usable for fixation (Schubert and Jahren 2012; Gamage et al. 2018). Besides, the stomatal conductance of the plant leaves decreases when the $p\text{CO}_2$ rises, which results in a lower p_i/p_a ratio and higher $\delta^{13}\text{C}$ signatures of C assimilates (see Eq. 1) (Farquhar et al. 1982; Gamage et al. 2018). Another study claims that mostly changing fractionation factors of the photorespiration and the conductance of the mesophyll lead to increasing isotopic signatures of plant tissues of about $0.014\text{‰} \pm 0.007\text{‰}$ ppm^{-1} (Keeling et al. 2017). Others predict a hyperbolic relationship between changes in $p\text{CO}_2$ levels and in fractionation during photosynthesis, with larger modifications in the degree of isotopic fractionation ($> 0.01\text{‰} \text{ppm}^{-1}$) when low $p\text{CO}_2$ levels ($\ll 450\text{‰}$) experience changes (Schubert and Jahren 2012, 2015). During the later Holocene, after 8 kyr BP the atmospheric $p\text{CO}_2$ increased from 260 ppm to 280 ppm (preindustrial times) (Elsig et al. 2009; Joos et al. 2004). The rise of $p\text{CO}_2$ during the last deglaciation has been calculated to cause a decrease

in the $\delta^{13}\text{C}$ signature of $1.4\text{‰} \pm 1.2\text{‰}$ for gymnosperms and $0.5\text{‰} \pm 1.5\text{‰}$ for angiosperms (Hare et al. 2018). A global increase of about 2.1‰ of the discrimination factor against ^{13}C of C3 plants has been computed by analysing $\delta^{13}\text{C}$ data from fossil leaves and bulk terrestrial organic matter from the last 30 kyr and explained by a rise in $p\text{CO}_2$ by 80 ppm from the Last Glacial to preindustrial times (Schubert and Jahren 2015).

All in all, the decreasing isotopic signature of atmospheric CO_2 (Suess effect) and its increasing concentration ($p\text{CO}_2$) have an important impact on the $\delta^{13}\text{C}$ signature of SOC because each has led to a depletion in the isotopic signature of new plant biomass inputs by about 2.0‰ and 1.8‰ respectively since industrialisation (1850) (calculated with data and equations from (Keeling et al. 2001; Rubino et al. 2019; Schubert and Jahren 2015) (Fig. 4). A tree ring chronology displays decreasing values of about 3.5‰ between 1850 and 2005, probably because of the increasing $p\text{CO}_2$ and decreasing $\delta^{13}\text{C}$ signature (Wang et al. 2011). Archived samples from wheat continuously grown on the same unfertilised field similarly show a significantly decreasing trend in the $\delta^{13}\text{C}$ signature over 153 years (1845–1997), which corresponds to the decreasing signature of atmospheric CO_2 , especially after 1960 (Zhao et al. 2001). The $\delta^{13}\text{C}$ signature of the grain and straw of wheat decreased by about 2.8‰ and 2.5‰ , respectively, whereas the signature of global atmospheric CO_2 decreased by only about 1.5‰ over that period. The remaining change can be explained by the increasing discrimination against ^{13}C because of rising $p\text{CO}_2$, alternating wheat cultivars and climatic changes of the precipitation amount and the temperature.

Changes in the environment

There are several factors influencing the $\delta^{13}\text{C}$ of plants through their effect on the p_i/p_a ratio (see Eq. 1), which is altered by the rate of diffusion of CO_2 into the leaves or the rate of CO_2 consumption by photosynthesis (Boutton 1996). Important environmental factors include irradiance, atmospheric $p\text{CO}_2$ (see [Changes in the concentration of atmospheric \$\text{CO}_2\$](#) section), vapour pressure deficit, soil moisture availability, soil salinity, soil fertility, air pollution, altitude, latitude and exposition, while

biological factors include photosynthetic capacity, plant development status, genetic variation, competition, growth form and life span (Fu et al. 1993; Boutton 1996; Kohn 2010). For example, the $\delta^{13}\text{C}$ signatures of plant biomass increase with better nitrogen (N) availability, because the intercellular CO_2 consumption is higher and the p_i/p_a ratio is lower when C-fixing enzymes and photosynthetic capacity are promoted by higher N contents in the leaves (Fu et al. 1993). Furthermore, the $\delta^{13}\text{C}$ signature of C3 plants is strongly correlated with mean annual precipitation because the discrimination against heavy isotopes is lower when stomata have to close more often to minimise water loss and the intercellular concentration of CO_2 (p_i) decreases (Madhavan et al. 1991; Farquhar et al. 1989; Kohn 2010). Isotopic $\delta^{13}\text{C}$ signatures of C3 plants above -25.5% can only be achieved in present environments with precipitation amounts $< 500 \text{ mm yr}^{-1}$ when plants experience water stress more often (Kohn 2010). A study observed decreasing $\delta^{13}\text{C}$ signatures (under less arid conditions) of -0.6% 100 mm^{-1} for C3 plants and -0.3% 100 mm^{-1} for C4 plants sampled along a precipitation gradient (25–600 mm) with an isotherm (Ma et al. 2012). They were also able to observe a related decrease in the isotopic signature of SOC (of the upper 2–3 cm) by about -0.4% 100 mm^{-1} for the precipitation range. Others found the $\delta^{13}\text{C}$ signatures of C3 plants grown in 75% air humidity to be 1.8–2.6% lower than in 30% air humidity, while C4 plants showed 0.8% higher isotopic signatures under moister conditions (Madhavan et al. 1991). For some C4 vegetation and plant species, no or a positive correlation with precipitation can be found (Ma et al. 2012; Swap et al. 2004). However, a substantial shift of up to 15% higher $\delta^{13}\text{C}$ signatures can occur when particular C3 plant species change their photosynthetic pathway to CAM (Crassulacean acid metabolism) in response to drought (Farquhar et al. 1989; Bloom and Troughton 1979). The latter is only of small and localised importance when these species are abundant. Increasing precipitation amounts, for example in Europe and western North America (Herzschuh et al. 2022) or in several regions of low latitudes (Braconnot et al. 2007; Rao et al. 2012) during the Holocene, could result in decreasing isotopic signatures of plants and formed SOC, which can contribute to local depth gradients of increasing

$\delta^{13}\text{C}$ signatures of SOC. Recently, climate change has increasingly been reducing water availability in many parts of the world, which leads to higher $\delta^{13}\text{C}$ signatures in plants (Canadell et al. 2021; Farquhar et al. 1989). This can be a future driver working against the commonly observed increasing $\delta^{13}\text{C}$ signatures of SOC with depth.

Sources of C inputs with different $\delta^{13}\text{C}$ signatures

The main input source of new SOC to the pedosphere are autochthonous plant assimilates that are released from plants during their decomposition and as root exudates or are exported to their mycorrhizal fungal partners. The $\delta^{13}\text{C}$ signatures of these C inputs depend on the photosynthetic pathway the plants use and on the plant organ which gets decomposed. Furthermore, organic carbon can enter the soil not only directly from plants, but also as allochthonous carbon due to anthropogenic activity or natural lateral transport. Furthermore, C can reach soils from the underlying parent material through weathering processes as geogenic C, from landscape fires as pyrogenic C, or through dark microbial C fixation.

C3 and C4 plant-assimilated C

Vegetation type, cropped plant species and agricultural practices change perpetually over time and affect the isotopic signature of SOC in soil profiles in many terrestrial systems (Basile-Doelsch et al. 2009; Trouve et al. 1994; Pessenda et al. 2010). Enrichments or depletions of $\delta^{13}\text{C}$ signatures of more than 10% can be found between surface soil and deep soil layers, probably due to temporal changes in the vegetation or, more precisely, the proportion of C3 and C4 plants (Fig. 5) (Martinelli et al. 1996; Mariotti and Peterschmitt 1994; Desjardins et al. 1991; Pessenda et al. 2010; Krull et al. 2005; Schneckenberger and Kuzyakov 2007; Trouve et al. 1994). The photosynthetic pathway of C3 plants leads to isotopic signatures of their biomass of between $\delta^{13}\text{C} = -20\%$ and -37% , whereas C4 plants show signatures of between $\delta^{13}\text{C} = -9\%$ and -17% (O’Leary 1988; Boutton et al. 1998; Kohn 2010). The mean isotopic difference between C3 and C4 plants is approximated to be about 14% (-27% vs. -13%), which is most clearly translated into $\delta^{13}\text{C}$ soil depth gradients when there is a complete vegetation change (C3/C4 or C4/

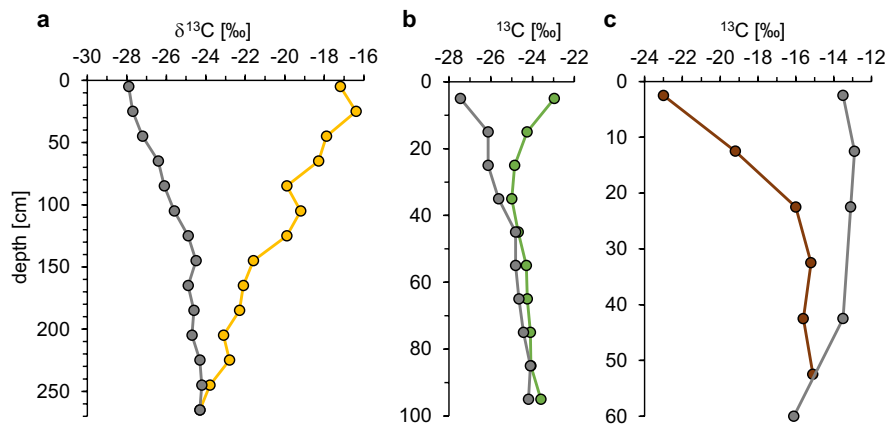


Fig. 5 Depth gradients of $\delta^{13}\text{C}$ signatures within soil profiles at sites with and without vegetation changes. Coloured lines show soil profiles after a vegetation change from C3 to C4 plants (a and b) or from C4 to C3 (c). **a** is drawn with data from (Pessenda et al. 2010) for two adjacent soil profiles in Brazil under a rainforest (REBIO V) (grey) and an open arboreal savannah ‘Tabuleiro’ (REBIO III) (yellow), which was

previously a rainforest. **b** is created with data from (Schneckenberger and Kuzyakov 2007) for soil profiles in Germany under a grassland (grey) and after 9 years of *Miscanthus* cultivation (green). **c** originates from (Trouve et al. 1994) and shows adjacent soil profiles in Congo under a savannah (grey) and a 21-year-old *Pinus* plantation (brown)

C3) and the SOC in the topsoil mostly consists of fresh C assimilates in contrast to the subsoil.

The $\delta^{13}\text{C}$ signature of SOC reflects the relative contribution of C3 and C4 vegetation to the community net primary productivity, and can serve as a proxy indicator of the development of vegetation and climate over time, because the geographical distribution of C4 plants is correlated with temperature and precipitation (Boutton et al. 1993; Osborne and Sack 2012; Rao et al. 2010). The main natural expansions of C4 plants in low and middle latitudes have occurred since the late Miocene (Rao et al. 2012) as an adaptation to improve the water and carbon acquisition of plants in an environment with decreased pCO_2 compared with the preceding Paleogene (Osborne and Sack 2012). C4 plants are better adapted to higher temperature environments, however an increase in pCO_2 in particular promotes C3 plants (Ehleringer and Cerling 2002). Rao et al. (2012) conclude that during the Holocene the proportion of C4 vegetation often decreases at low latitudes because of increasing precipitation, while at middle latitudes the proportion of C4 vegetation increases because of rising temperatures. The vegetation changes at low latitudes can be a factor leading to greater increases in the $\delta^{13}\text{C}$ signatures of SOC with depth, while at middle latitudes these

changes can attenuate isotopic depth gradients. However, since changes in the precipitation amount and temperature during the Holocene are not uniform at different latitudes and on different continents (Braconnot et al. 2007), their influences on the vegetation and thus on the depth gradient of the $\delta^{13}\text{C}$ signature of SOC must be individually assessed for each site. Currently C4 plants account globally for approximately 20% of terrestrial gross primary production (Beer et al. 2010) and have their highest abundances on savannahs and grasslands between 30–40 °N and 15–25 °S (Bird and Pousai 1997; Rao et al. 2010). At high latitudes above 60 °N and below 46 °S, C4 plants are and have mostly been absent because the temperatures are too low (Rao et al. 2012), so natural vegetation changes should have minor effects on the depth gradients of $\delta^{13}\text{C}$ signatures there. The vegetation also changes due to human activities (e.g. arable farming, forestry or livestock) (Boutton et al. 1993; Basile-Doelsch et al. 2009). For example, livestock grazing can promote C3 grass over C4 vegetation in tallgrass prairie and can result in more depleted $\delta^{13}\text{C}$ signatures of the SOC than on ungrazed sites in the upper 90 cm of soil (Boutton et al. 1993). In contrast, the introduction of C4 plants such as maize in arable fields at higher latitudes is a factor leading to higher isotopic

signatures of newly formed SOC and lower $\delta^{13}\text{C}$ gradients within soil profiles (Schneider et al. 2021).

Above- and belowground C inputs

The average maximum rooting depth of different biomes ranges from 0.5 m for tundra to 15 m for tropical grassland and savannah (Canadell et al. 1996) and determines the location of belowground C inputs. The rooting depths of different plant species could affect the $\delta^{13}\text{C}$ signatures within soil profiles if their isotopic signatures of the rhizodeposits deviate from that of above ground litter. The roots of C3 plants commonly show enriched isotopic signatures of about 1.2‰ compared to the leaves, while the roots of C4 plants often have smaller enrichments of 0.4‰ (Bird et al. 2003; Werth and Kuzyakov 2010). It was demonstrated that the respired CO_2 of C3 plant leaves and of the roots of woody species is commonly enriched in ^{13}C , while the respiration of the roots of herbaceous species is commonly depleted; both leading to post-photosynthetic fractionations (Ghashghaie and Badeck 2014). This could promote an enrichment of the roots of herbaceous C3 plants compared to their leaves besides the influences of deviating biochemical compositions, diel carbohydrate dynamics and other possible factors reviewed by Cernusak et al. (2009). A rapid rise of the $\delta^{13}\text{C}$ signature of 0.5–1.0‰ with increasing soil depth within the upper 10 cm could be therefore promoted by an increasing proportion of root-derived C and a lower above ground litter derived fraction (Bird et al. 2003) along with effects of preferential degradation. Additionally, vegetation changes can result in variations in the depth of C inputs. Especially in the boreal and temperate zone, there was a succession of tree species across the landscape after the last ice age until it was mostly forest-dominated. It could be assumed that ancient root-derived carbon in the subsoil can evoke a difference between the isotopic signatures of the SOC in the top- and subsoil. But as cold and temperate forest ecosystems show higher isotopic discriminations during photosynthesis than temperate grasslands (Kaplan et al. 2002), such vegetation changes might be a driver against increasing $\delta^{13}\text{C}$ signatures with depth.

Pyrogenic C

Another C input to soils is pyrogenic carbon, which is produced by the burning of biomass. Around 12% of emissions from landscape fires are buffered by the production of pyrogenic C, which accumulates in soils because of its high recalcitrance (Jones et al. 2019). Pyrogenic C comprises on average 14% of total SOC and clay-rich soils can even store >30% of total SOC as pyrogenic carbon (Reisser et al. 2016). The isotopic signature of pyrogenic C largely reflects the signature of the source, but can deviate by about $\pm 2\%$ depending on the burning temperature (Bird and Ascough 2012). An effect of pyrogenic C on the isotopic signature of SOC only appears in environments where fires are frequent at least during one time interval of pedogenesis. Soil $\delta^{13}\text{C}$ depth gradients could be affected if the proportion of pyrogenic C to bulk SOC changes within the soil profile and the isotopic signature of pyrogenic C differs from that of the bulk SOC.

Dark microbial fixed C

Most microorganisms in the soil are chemoorganoheterotrophs and use organic molecules as their C and energy source (Kästner et al. 2021; Delgado-Baquerizo et al. 2018). However, besides photoautotrophs certain prokaryotic taxa are capable of directly fixing inorganic C chemoautotrophically or anaplerotically, which might result in $\delta^{13}\text{C}$ signatures of the biomass of the latter closer to the atmospheric source than photosynthetically assimilated C (Nel and Cramer 2019). The enzymes active in the anaplerotic pathway mainly accept the inorganic C phase of HCO_3^- , which can be substantially enriched in ^{13}C by up to 7–11‰ in comparison with CO_2 because of the temperature-dependent fractionation during its hydrogenation (Mook et al. 1974; Zhang et al. 1995). Such anaplerotic fixation can lead to higher $\delta^{13}\text{C}$ signatures in microbial biomass and is further influenced by the fraction of atmospheric CO_2 in the upper soil layers, which has a higher ^{13}C content than soil CO_2 derived from respiration (Nel and Cramer 2019). Furthermore, the soil CO_2 around the soil organism is enriched in ^{13}C in comparison with soil-respired CO_2 due to the different diffusion coefficients of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ out of the soil, which can

result in a depletion of soil-respired CO_2 of 4.4‰ (Cerling et al. 1991). The fixation of inorganic C by some microorganisms can be used to maintain metabolic activity under C-poor conditions (Šantrůčková et al. 2018). The rates of dark microbial C fixation are small compared with soil respiration rates (1.2–3.9% of the respiration) and even with the fixation rate of photoautotrophic soil surface microbes (Spohn et al. 2020; Delgado-Baquerizo et al. 2018; Schmidt et al. 2016). Dark microbial C fixation could increase $\delta^{13}\text{C}$ signatures of SOC in particular environments where heterotrophic metabolism is slow or where inorganic C provides the dominant basis for the microbial community, for example in deep arctic or hyper-arid soils (Šantrůčková et al. 2018; Ji et al. 2017).

Allochthonous C

Anthropogenic modifications, such as deep ploughing, landfills, plaggen soil and mining, shift and bury large amounts of topsoil C into the subsoil (Schneider et al. 2021). Historic heathland and peatland cover of agricultural soils influences the quality, quantity and isotopic signature of the stored SOC (Schneider et al. 2021). Another allochthonous input of C into the soil system is the use of organic fertilisers. Animal manure can be depleted in comparison with animal feed (plant materials) by about 0.3‰ (Bol et al. 2005; Kristiansen et al. 2004). A significant decrease in the $\delta^{13}\text{C}$ signature of SOC in the topsoil was observed after 37 years of manure application because it had a lower $\delta^{13}\text{C}$ signature than the original SOC (Gerzabek et al. 1997). Another long-term field experiment with different fertilisation regimes found the C content and $\delta^{13}\text{C}$ signature of SOC in the upper 20 cm to be similar, irrespective of the usage of animal manure or mineral fertiliser, probably because the amount of the manure was much smaller than the residues of the crops (Bol et al. 2005). It can be concluded that organic fertilisers only change the $\delta^{13}\text{C}$ signature of SOC when the applied amount is high and the isotopic signature of animals' diet differs significantly from that of crops on the field.

Geogenic C

Geogenic organic carbon (GOC) is bedrock derived C and can affect the SOC isotopic signature in

the subsoil. Sedimentary bedrocks can contain 0.1–0.3 g kg⁻¹ GOC and are widespread over 65% of the terrestrial earth surface (Amiotte-Suchet et al. 2003; Kalks et al. 2021). The effect on the SOC isotopic signature is determined by the amount of the GOC in the bedrock, the rate of turnover of this GOC, the quantity of SOC, and the difference between the isotopic signatures of SOC and GOC (Kalks et al. 2021). GOC potentially has a $\delta^{13}\text{C}$ signature different to that of modern vegetation because of lower pCO_2 , higher $\delta^{13}\text{C}$ signatures of atmospheric CO_2 and climate conditions during C fixation that differ from those found today. Allochthonous C in colluvial or alluvial Holocene deposits from upstream or upslope can enhance C amounts in subsoils substantially, while C from aquatic sources can lead to depleted isotopic signatures of organic C in Holocene parent materials (Schneider et al. 2021). If C compounds are incorporated into sediments under marine conditions, the isotopic signature of plankton is the most important, while under continental conditions the detritus of higher plants affects the isotopic signature of the organic C in the sediments (Deines 1988). Carbon in sedimentary rocks has been termed kerogen, and consists of coal-like particles of amorphous C formed by compaction and dewatering during diagenesis. The isotopic signature of these kerogens is not only influenced by the C sources, but also by the fractionation due to the transformation from plant tissue to organic matter and diagenetic changes in the sediment (Deines 1988).

Internal processes affecting the $\delta^{13}\text{C}$ signatures of SOC

Organic C compounds become decomposed, transformed, translocated and stabilised within the soil profile by soil-internal processes (see Fig. 2). Carbon components with various chemical structures, physical shapes (of particulate organic matter) and isotopic signatures can be translocated and stabilised along the soil profiles. When new organic material enters the soil, the balance between microbial priming and microbial entombing affects the organic material's fate in the soil (Liang et al. 2017). The influence of a preferential decomposition (catabolism) and physico-chemical stabilisation of SOC on compounds with

specific isotopic signatures and the effects of microbial biomass synthesis (anabolism) are discussed below. Furthermore, the transport of DOC is discussed in relation to its impact on the isotopic signature of SOC.

Preferential C turnover and physico-chemical stabilisation

Preferential C turnover

During initial decomposition stages (leaf senescence, litterfall and SOC formation) an enrichment of the remaining organic material with ^{13}C by 1.7–2.9‰ was observed irrespective of the vegetation type (Buchmann et al. 1997). This is supported by the observation of depleted isotopic signatures of evolving CO_2 during the initial decomposition processes (Kristiansen et al. 2004). In contrast, other incubation experiments found for initial decomposition stages respired CO_2 from plant litter to be depleted ^{13}C in comparison with the litter but to be enriched after more than a week of incubation (Schweizer et al. 1999; Fernandez et al. 2003). The depletion of the respired CO_2 in the first stage of the initial decomposition could be because of a kinetic fractionation effect by highly active microbes, when the energy availability and nutrient status of the C compounds are high (Feng 2002; Fernandez et al. 2003). It could likewise be related to a turnover of microbial biomass if the microbes have used depleted C sources compared to the freshly added substrate prior to the addition (Blagodatskaya and Kuz'yakov 2008). In the later stage of the initial decomposition of litter, the preferential usage of enriched substrates such as cellulose or enriched microbial necromass could be responsible for the observed increase in the isotopic signature of the respired CO_2 (Fernandez et al. 2003; Prescott and Vesterdal 2021). All in all, the changing $\delta^{13}\text{C}$ signatures of the remaining C compounds during the initial decomposition stages can be explained by time-dependent opposing factors: enrichment by the kinetic isotope fractionation of microbial respiration and depletion caused by preferential decomposition (Balesdent and Mariotti 1996; Feng 2002; Fernandez et al. 2003). In general aging of organic matter results in ^{13}C enrichments. However, others have observed non-directional changes of $<0.5\%$ in the isotopic signature of leaf litter from tree and shrub species

during the first year of decomposition although half of the litter mass was lost (Boutton 1996). Carbon decomposition and transformation was even investigated in long-term bare fallow experiments that did not receive any fresh litter input. An increase of 0.4‰ in the $\delta^{13}\text{C}$ signature in the topsoil SOC was found when soils lay bare without vegetation for 37 years (Gerzabek et al. 1997). Another long-term experiment with bare fallow found an enrichment in ^{13}C of 0.008–0.024‰ per year and an absolute increase of 2.0‰ in an 80-year period, during which 65% of the SOC was lost (Menichetti et al. 2015). An enrichment of the remaining material in ^{13}C is in line with the observed trend of increasing $\delta^{13}\text{C}$ signature with soil depth, because the proportion of transformed C compounds is higher in the subsoil than in the topsoil.

Different parts of plant materials, litter fractions and SOC compounds deviate in their $\delta^{13}\text{C}$ signature relative to the bulk material, which can have an effect on the isotopic signature of the remaining SOC and respired CO_2 when a preferential turnover of selected compounds takes place (Benner et al. 1987; Schweizer et al. 1999; Bowling et al. 2008). Several plant tissues show different isotopic signatures, for example the roots of legumes are enriched by about 1.5‰ in comparison with their leaves (Schweizer et al. 1999) and grains of wheat show on average a 1.9‰ higher isotopic signature than straw (Zhao et al. 2001). Isotopic signatures often deviate because of the distinct chemical compounds that form the cell structures of different plant tissues. Lipids are depleted in ^{13}C while pectin tends to be enriched (Deines 1988). The cellulose and hemicellulose fractions are enriched by 1–2‰ relative to the whole plant material, whereas the lignin fraction is commonly depleted by 2–6‰ in comparison with the bulk material (Benner et al. 1987; Schweizer et al. 1999). Selective preservation of lignin is mostly relevant in the initial decomposition stages of litter (Kalbitz et al. 2006), but the chemical composition does not determine the long-term fate in soils (Marschner et al. 2008; Heim and Schmidt 2007; Prescott and Vesterdal 2021). Thus, the initial stages of litter decomposition provide few insights into the long-term persistence of organic compounds and the development of the isotopic signatures of C deeper than the litter layer. Physical protection, chemical interactions of organic compounds with mineral surfaces and biological factors determine the stabilisation, turnover and transformation

of SOC (Schmidt et al. 2011; Marschner et al. 2008), and thus impact the $\delta^{13}\text{C}$ signature of SOC. In the long term, microbial C recycling could play a greater role and contribute to increasing $\delta^{13}\text{C}$ signatures with time and depth (see [Microbial C recycling](#) section) (Balesdent and Mariotti 1996). Differentiation between a preferential usage of C compounds and fractionation effects during microbial metabolism remains a challenge.

Physico-chemical stabilisation of C in the soil profile

The chemical structure of organic molecules is found to be important only during early decomposition and not for long-term stabilisation, because most SOC of natural origin can be metabolised by highly adapted microbial communities (Dungait et al. 2012; Lützow et al. 2006; Schmidt et al. 2011; Ruiz-Dueñas and Martínez 2009). Specific chemical structures and compounds may, however, influence its turnover, such as pyrogenic C from incomplete combustion (see [Pyrogenic C](#) section) or plant phytoliths (PhytOC) that have promoted C stabilisation for hundreds to millions of years (Lorenz et al. 2007; Parr and Sullivan 2005; Kirschbaum et al. 2021). Compounds can resist mineralisation processes when they provide a small energetic yield relative to the energy amount required for synthesis of the enzymes targeting them (Henneron et al. 2022). Plant phytoliths are plant opals containing silica and on average 1% C, and can be stabilised in soils because of their high recalcitrance, with accumulation rates of around $18 \text{ g C m}^{-2} \text{ yr}^{-1}$ in sugarcane fields for example (Parr and Sullivan 2005; Basu et al. 2015). The isotopic signature of newly formed PhytOC is depleted by about 13‰ in comparison with the source plant in the case of C4 plants and show nearly the same signature as the plant when a C3 plant is the source (Basu et al. 2015). In most soils, however, the amount of PhytOC is expected to be too small to impact the bulk SOC isotopic signatures, especially in the topsoil.

Physical inaccessibility to microbial communities through occlusion within aggregates, organo-mineral interactions and relocation in deeper soil horizons, which are often waterlogged, anoxic, cold and nutrient-limited, determine the long-term stabilisation of C (Kopittke et al. 2018; Dungait et al. 2012). Carbon compounds reaching deep soil layers are probably

better protected from decomposition because the rate of microbial catabolism decreases substantially with depth (Fontaine et al. 2007). The soil texture can determine the SOC turnover rate, whereby coarse-textured soils demonstrate faster turnover rates (Boutton et al. 1993). This can ultimately affect the steepness of the $\delta^{13}\text{C}$ depth gradient. For example, in a coarse-textured soil, the $\delta^{13}\text{C}$ signature of the SOC increased by 1.3–1.6‰ from the topsoil to 100 cm soil depth compared with a fine-textured soil with a much larger $\delta^{13}\text{C}$ gradient of 3.8–5.8‰ (Wynn et al. 2005). Mineral-associated organic carbon (MAOC) was found to originate more from fungal residues than from plant residues (Klink et al. 2022) and to have a 1–3‰ higher $\delta^{13}\text{C}$ signature than the plant C inputs (Torn et al. 2009). Kinetic fractionation during decomposition of C compounds may result in preferential accumulation of ^{13}C . The higher the degree of stabilisation, the longer the transformation time and ultimately thus the higher the ^{13}C signature (Wynn et al. 2005). The stabilisation of higher amounts of ^{13}C -enriched microbial necromass in fine-textured soils could be a reason for the stronger gradients in these soil types (see [Microbial C recycling](#) section) (Ni et al. 2020).

Microbial C recycling

Microorganisms mediate both the mineralisation and formation of SOC (Kästner et al. 2021). Just a slight fractionation during microbial transformation processes can cause a significant enrichment of the remaining SOC since the C fraction remaining in the soil is small compared with the total C inputs (Högberg et al. 2005). Most studies have found the biomass of microbes and other soil biota to be enriched by >2‰ relative to the SOC in the topsoil due to anabolic processes (Dijkstra et al. 2006; Šantrůčková et al. 2000; Gleixner et al. 1993; Potthoff et al. 2003; Briones et al. 1999). While the microbial biomass comprises less than 5% of the SOC (Dalal 1998), the necromass (dead microbial biomass) contributes about 51, 47 and 35% to the SOC in the topsoil of croplands, grasslands and forests, respectively (Wang et al. 2021). Microbial recycling of building blocks (e.g. amino acids, amino sugars, mono- and oligomers of fatty acids, nucleotides) from microbial necromass could provide the resources for microbial growth cycles (Kästner et al. 2021). This is expected

to result in steady ^{13}C enrichment during the continuous recycling of microbial necromass, which is preferentially used because it is energetically favourable to incorporate pre-existing compounds to biomass rather than synthesise new compounds. Even though the abundance of microorganisms is often higher in the topsoil than in the subsoil (Hicks Pries et al. 2018), their proportion of SOC is smaller in the topsoil because of the high input of plant-derived C compounds. Therefore, the impact of the microbial biomass and necromass on the $\delta^{13}\text{C}$ signature of the SOC is greater in the subsoil. Not only the proportion to SOC, but also the isotopic signature of microbial biomass changes within soil profiles promoting enrichments in ^{13}C with depth. A study found increasing $\delta^{13}\text{C}$ signatures of 7.6–8.4‰ of the microbial biomass (indicated by phospholipid fatty acids; PLFA) with soil depth (from organic L layer to the mineral B horizon) (Kohl et al. 2015). The concentration of PLFA and the isotopic signatures of specific fungal and bacterial PLFA were nearly constant over depth, but the fungi/bacteria ratio decreased. The latter can explain the increase in the $\delta^{13}\text{C}$ signature of the PLFA within the soil profile in this case because the fungi showed lower $\delta^{13}\text{C}$ signatures than the bacteria and the bulk SOC (Kohl et al. 2015). This could be caused by some fungi being specialised degraders of lignin that is ^{13}C depleted (Osono 2007; Benner et al. 1987). Another study also found an increasing share of bacterial necromass in total SOC with depth from 12% at 0–20 cm depth to 39% at 50–100 cm depth, while the proportion of fungal necromass remains constant at between 19 and 23% (Ni et al. 2020). All in all, the bacteria-dominated microbial biomass and necromass in subsoils could promote the formation of the isotopic soil depth gradient with an increase of 2.8‰ (Kohl et al. 2015). Furthermore, land-use type can affect the fungi/bacteria ratio of the necromass, which is higher in forest topsoils than in arable soils and grasslands (Kohl et al. 2015; Liang et al. 2019). A higher $\delta^{13}\text{C}$ signature in the subsoil could also be promoted by the leaching of microbial products as DOC (see [Translocation of DOC](#) section) and a higher relative contribution of microbe-derived C relative to plant-derived C (Boström et al. 2007; Ehleringer et al. 2000; Kaiser and Kalbitz 2012).

The C input via mycelia can be an important pathway for C entering the soil, and can exceed

the input via litter and fine root turnover (Godbold et al. 2006). A study has found that on average more than 40% of the SOC consists of fungal necromass and only 15% of bacterial necromass in the upper 25 cm of agricultural and grassland topsoils (Liang et al. 2019). The $\delta^{13}\text{C}$ signature of the biomass of saprophytic fungi can deviate by $\pm 2.5\%$ from their substrates (Abraham and Hesse 2003). In a greenhouse experiment, the hyphae of arbuscular mycorrhizal fungi were observed to be enriched in ^{13}C by 1–6‰ in comparison with their host plants (Walder et al. 2012). Fruit bodies of host-specific ectomycorrhiza had a 1.2–2.9‰ higher $\delta^{13}\text{C}$ signature than the foliar samples from their host trees (Högberg et al. 1999). However, this is not necessarily a result of a fractionation process because ectomycorrhizal fungi are often facultative saprotrophs that utilise both plant and SOC-derived compounds for growth (Hobbie et al. 2001; Kuyper 2016). The effect of fungi on the isotopic signature of SOC within soil profiles remains equivocal, although fungal necromass is an important component of SOC (Liang et al. 2019). In general, the biomass of microorganisms and other soil biota tends to be ^{13}C enriched relative to the SOC pool, with a direct influence on the depth gradient of the isotopic signature of SOC within soil profiles due to the increasing proportion of microbial recycled SOC with soil depth.

Methanogenesis and methanotrophy

The metabolism of methanotrophs and methanogens could have an impact on the isotopic signatures of SOC, especially in wet soils with anoxic layers. Methanogenic archaea generally live under anoxic conditions (Penger et al. 2012), but methanogens also exist in oxygenated soils, probably located within anaerobic microsites of soil aggregates (Angle et al. 2017). In general, methane is produced by archaea in deep, anoxic soil layers and reaches $\delta^{13}\text{C}$ signatures of $-55.9 \pm 4.2\%$ in rice paddies for example (Uzaki et al. 1991). Methylotrophic methanogens produce CH_4 with a $\delta^{13}\text{C}$ signature up to 80% lower than their substrate, whereas hydrogenotrophic methanogens show a fractionation of 22–58%, and acetoclastic methanogens display a fractionation of $< 5\%$ against the model substrate acetate, all depending on temperature (Valentine

et al. 2004; Penger et al. 2012). Reaction equations of the anaerobic degradation of carbohydrates predict that one third of the methane is produced by hydrogenotrophs fuelled by hydrogen and CO_2 , and two thirds by acetoclastic methanogens using acetate as a substrate (Conrad 1999), but the proportion of hydrogenotrophs to methane production can be even higher (Lansdown et al. 1992). Due to the strong discrimination against ^{13}C during methane production by methanogens, the remaining unconsumed dissolved CO_2 can reach signatures above 5‰ (Dorodnikov et al. 2022). It is possible that the biomass and necromass of the archaea are isotopically enriched and accumulate within anoxic soil layers. However, actual measurements show no trends of increasing $\delta^{13}\text{C}$ signatures in deep anoxic peat (Rask and Schoenau 1993; Alewell et al. 2011), suggesting that additional factors are involved. It can be concluded that methanogenesis has a small overall influence on bulk SOC isotopic signatures due to low absolute amounts of produced methane in most soils, except for wetlands. But even in these ecosystems anaerobic mineralisation may barely affect the isotopic signatures of SOC, because of the huge overall SOC content, for example in peatlands.

The opposite process is methane oxidation, which occurs in most aerobic soils via methanotrophs (Le Mer and Roger 2001). These methane-oxidising bacteria (MOB) prevent emissions to the atmosphere from methanogens and also take up methane from the atmosphere, making soils an important biological methane sink (Le Mer and Roger 2001; Ho et al. 2019). Methanotrophs preferentially use light C isotopes of the already isotopically depleted methane (Barker and Fritz 1981). Extremely depleted $\delta^{13}\text{C}$ signatures of -42‰ are observed in Early Triassic paleosols, probably because of significant amounts of SOC derived from methanotrophic biomass during this time (Krull and Retallack 2000). Besides the conversion to CO_2 , about 7% of the consumed CH_4 can be transformed into organic acids and 40% into microbial biomass (Khanongnuch et al. 2022), which could lower the isotopic signature of topsoil SOC. The effects of methanotrophs on the $\delta^{13}\text{C}$ signature of SOC are generally low in most soils because of their small population sizes relative to heterotrophic microorganisms, even though fractionation effects are relatively large (Krull and Retallack 2000). All in all, methanogenesis and methanotrophy are processes that

should promote steeper depth gradients of the $\delta^{13}\text{C}$ signatures of SOC because of the upward translocation of ^{12}C as depleted CH_4 . But in wetlands, where these processes are most powerful depth gradients are small (see [Examples of \$\delta^{13}\text{C}\$ gradients of several soil profiles and general interpretation guidelines](#) section) (Alewell et al. 2011).

Translocation of DOC

Translocation of C from topsoil to subsoils mostly occurs by illuviation as dissolved organic carbon (DOC) or by bioturbation (Schneider et al. 2021). The DOC is typically derived from rhizodeposits, breakdown of SOC or products of microbial necromass (Trumbore et al. 1992). The mobility of DOC through the soil column is higher than that of particulate C because of its small size ($<0.45\ \mu\text{m}$), which decreases physical restrictions. Nevertheless, the transport of DOC within a soil profile is a complex process involving temporal immobilisation, microbial processing, subsequent desorption and dissolution (Kaiser and Kalbitz 2012). Philben et al. (2022) could not identify any significant difference between the isotopic signature of SOC and DOC percolation from the organic topsoil layer of a forest ecosystem and hypothesized that DOC does not impact the $\delta^{13}\text{C}$ gradients within soil profiles. But others showed that in the topsoil, the amount of plant-derived DOC is higher, whereas in the subsoil microbe-derived DOC is more abundant and therefore often enriched in ^{13}C (Kaiser and Kalbitz 2012; Högberg et al. 1999; Briones et al. 1999). Kaiser et al. (2001) further observed an accumulation of the hydrophilic DOC fraction with depth when water moves vertically through the soil profile. Hydrophilic DOC is enriched in ^{13}C compared with the hydrophobic DOC fraction and leads to an enrichment in ^{13}C with soil depth. Mineral surfaces preferentially sorb hydrophobic substances, such as depleted lignin-derived compounds, leading to an enrichment of the average $\delta^{13}\text{C}$ signature of compounds remaining in the soil water (Kaiser et al. 2001). Changes to the isotopic signature of DOC are primarily due to the relative proportion of hydrophilic and hydrophobic compounds determined by their mobility, which could contribute to the enrichment of $\delta^{13}\text{C}$ signatures of SOC with soil depth.

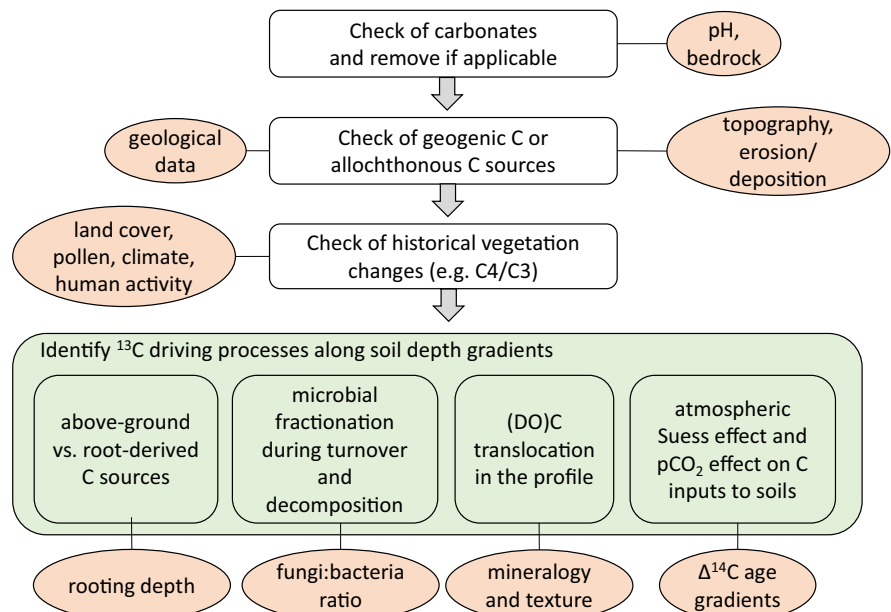
Examples of $\delta^{13}\text{C}$ gradients of several soil profiles and general interpretation guidelines

Soil depth gradients of the $\delta^{13}\text{C}$ signature of SOC can be used to identify vegetation changes and soil processes that affect C compounds. However, due to the simultaneous impact of multiple factors, their interpretation is often hampered and requires care. The interpretation must be specific to the pedo-climatic conditions and the soil type. To identify soil processes several major factors impacting $\delta^{13}\text{C}$ signatures and the soil $\delta^{13}\text{C}$ depth gradients need to be checked first in order to exclude them as drivers. In the following figure we summarize some steps that should be considered when analysing depth gradients of the $\delta^{13}\text{C}$ signature of SOC and describe which additional data could be useful for an adequate interpretation (Fig. 6).

In the following, we want to give some examples of depth gradients of the $\delta^{13}\text{C}$ signature of SOC for several soils to illustrate the soil type and site-specific context that always need to be accounted when interpreting such data. Histosols often show slightly decreasing or uniform $\delta^{13}\text{C}$ signatures with depth, possibly because of the stabilisation of C under anaerobic, waterlogged conditions and the lower microbial fractionation (Krull and Retallack 2000; Alewell et al. 2011; Freeman et al. 2001).

Anaerobic mineralisation could elevate the proportion of isotopically depleted organic substances such as lignin in the remaining C fraction without a kinetic isotope fractionation and preferential release of ^{12}C , as observed during aerobic turnover (Benner et al. 1987; Alewell et al. 2011). This could be a driver for lower $\delta^{13}\text{C}$ signatures in deep anoxic peat layers (Fig. 7). Environmental drivers, such as moisture availability (Xia et al. 2020) or the Suess effect on the isotopic signature of C assimilated by *Sphagnum* mosses and the depth of the groundwater table (100 cm), could explain the increase in the $\delta^{13}\text{C}$ signature in the upper 100 cm of the illustrated example (Estop-Aragonés 2022). Furthermore, Gleysols show more negative $\delta^{13}\text{C}$ signatures in groundwater-influenced horizons than other soils with aerobic conditions at similar depths, possibly due to the preservation of plant materials under anoxic conditions or the influence of allochthonous C from aquatic sources in the Holocene parent material with depleted isotopic signatures (Schneider et al. 2021). Likewise, mineral arable soils with a mean groundwater table shallower than 80 cm show 1.4‰ lower $\delta^{13}\text{C}$ signatures at 70–100 cm depth than soils with a mean groundwater table deeper than 200 cm (Schneider et al. 2021). Even in the topsoil of these soils where the groundwater does not affect the degradation of SOC, the $\delta^{13}\text{C}$ signature of SOC is more depleted

Fig. 6 Interpretation guidelines for analysing soil depth gradients of the $\delta^{13}\text{C}$ signature of SOC



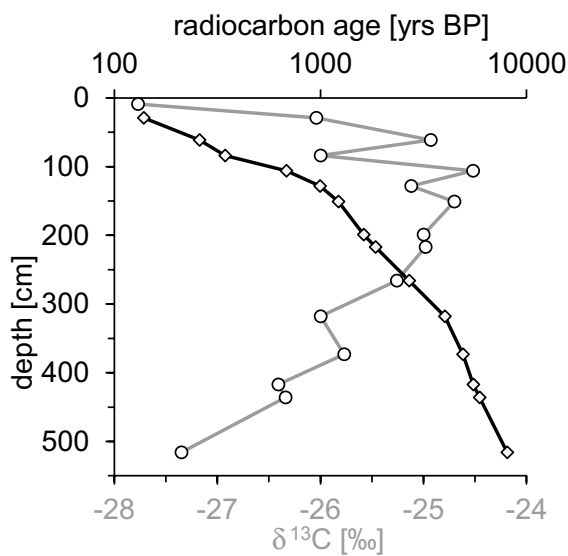


Fig. 7 Depth gradients of the $\delta^{13}\text{C}$ signature of soil organic carbon and the radiocarbon age in a mature thermokarst bog in northern Alberta, Canada. The grey line shows the depth gradient of the $\delta^{13}\text{C}$ signature and the black line shows the radiocarbon age in years before present (logarithmic scale). Data originate from Estop-Aragonés (2022)

probably because plants are under water stress less often when groundwater tables are high, leading to more depleted isotopic signatures of C3 plants and SOC in the topsoil (Schneider et al. 2021; Boutton 1996).

Mature boreal forests show particularly steep depth gradients of $\delta^{13}\text{C}$ signatures of about 3–4‰ from the organic to the underlying mineral soil horizons (Högberg et al. 2005). This can be explained by a combination of a high accumulation of fresh, depleted, plant-derived SOC and a high fungi/bacteria ratio in the topsoil and organic layer and the leaching of enriched hydrophilic DOC. The high depth gradient could be also promoted by a higher proportion of root-derived SOC in the subsoil than in the topsoil, if the $\delta^{13}\text{C}$ signature of the roots of the woody plants is higher than that of the litter and of herbaceous plants at the soil surface (Philben et al. 2022).

There are also sites where $\delta^{13}\text{C}$ signatures decrease with depth like in two Australian Vertisols (Krull and Skjemstad 2003). The authors explained the gradients by the stabilisation of depleted alkyl C in a low pH environment with clay-rich minerals. Such negative ^{13}C trends could also be due to

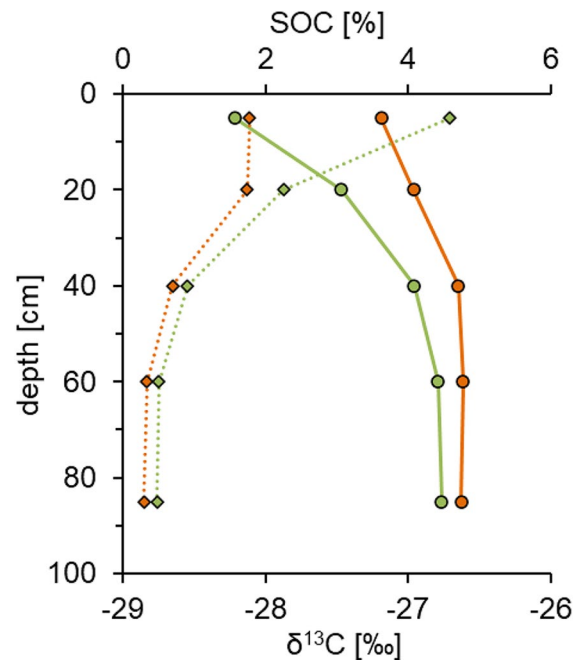


Fig. 8 Average depth gradients of $\delta^{13}\text{C}$ signatures (solid lines) and organic carbon content (dashed lines) in German agricultural soils for croplands (orange) and grasslands (green), adapted from Schneider et al. (2021)

a temporally increasing proportion of C4 over C3 plant vegetation. In particular in agricultural topsoils, the isotopic $\delta^{13}\text{C}$ signature is affected mostly by land use and C4 plants in crop rotation, with maize and other C4 cropping reducing the depth gradient of the $\delta^{13}\text{C}$ signatures by elevating the topsoil $\delta^{13}\text{C}$ signatures (Schneider et al. 2021). In general, it has been shown that the $\delta^{13}\text{C}$ signature of SOC increases on average by 1.5‰ in German grasslands within 100 cm, and only by about 0.7‰ in croplands without maize cultivation (Fig. 8). The low depth gradient of croplands, which can be observed even without the cultivation of C4 plants, could be explained by a homogenising of the SOC with tillage in the plough layer. Tillage makes the impacts of the Suess effect and the effect of increasing pCO_2 fuzzy, which are otherwise most dominant in the upper 30 cm of the soil profile. Another reason for the low depth gradients could be the low incorporation of fresh organic C compounds into the soil due to the removal of large biomass fractions with agricultural products (Smith et al. 2007).

A comparison can be made between the depth gradients of the $\delta^{13}\text{C}$ signature of SOC in archived pre-industrial soil cores and modern soil cores, allowing the exclusion of the effects of changing isotopic signatures of atmospheric CO_2 on the plant-derived C inputs. Torn et al. (2002) found similar soil depth gradients of $\delta^{13}\text{C}$ signatures increasing by 2‰ within one metre in an archived soil core (from about 1900) and a modern soil core from the same site in a Russian steppe. They observed that C stocks have not changed significantly over the last 100 years, and that the depth gradient of the $\delta^{13}\text{C}$ signature was similar in both cores and could thus not be attributed to the Suess effect (Torn et al. 2002). It should be considered that the soil under a steppe vegetation stores high amounts of C and the small proportion of the newly formed C may have only a minor effect on the $\delta^{13}\text{C}$ of bulk SOC. Thus, the results cannot be generalised to other sites. The study nevertheless shows that the trend in $\delta^{13}\text{C}$ signature with depth also arises without the Suess effect and that other drivers must also be of importance. The isotopic enrichment with ^{13}C within the pre-industrial soil core could be caused by changing $\delta^{13}\text{C}$ signatures of plant C inputs through vegetation shifts and changes in the amount of precipitation or could be related to soil processes such as the accumulation of ^{13}C -enriched bacterial necromass in the subsoil. Pollen records can be used (if existing) in combination with $\delta^{13}\text{C}$ data to identify vegetation changes (Rao et al. 2012) and separate this driver from the other internal and external drivers and processes affecting the $\delta^{13}\text{C}$ signature of SOC within soil profiles.

Conclusions and outlook

In general, the Suess effect, the effect of increasing atmospheric CO_2 concentrations, the distribution pattern of microbial necromass (fungi/bacteria ratio) in the soil column, and the translocation of enriched hydrophilic DOC in the subsoil are ubiquitous factors that enhance the $\delta^{13}\text{C}$ signatures of SOC with depth in most soil profiles. Other factors are time-dependent, such as fractionation during decomposition stages, or site-specific, such as the effects of changing precipitation and vegetation composition or the contribution of geogenic and allochthonous C to SOC. Vegetation changes can dominate the depth gradients of $\delta^{13}\text{C}$ signatures

when C4 plants replace C3 plants or vice versa (about $\pm 14\text{‰}$). This can be much higher than the Suess effect (about 2.0‰), the effect of increasing atmospheric CO_2 (about 1.8‰) or environmental effects on the photosynthetic ^{13}C fractionation (up to $\pm 3\text{‰}$). Likewise, the variation in the proportion of enriched necromass to SOC and its fungi/bacteria ratio as well as the leaching of enriched DOC can lead to additional increases in the isotopic signature of up to 3‰. Aspects such as preferential decomposition, lower $\delta^{13}\text{C}$ signatures of atmospheric CO_2 in the early Holocene relative to the preindustrial signature, and the effects of drier or more nutritious conditions on plant photosynthesis are in contrast with the commonly observed enrichment of ^{13}C with soil depth. However, these are of relatively subordinate importance in most soil profiles. External drivers, such as changes in atmospheric and climate conditions, are increasing in their importance and seem to be stronger in shaping the $\delta^{13}\text{C}$ depth gradients than internal soil processes.

Future interpretations of depth gradients of $\delta^{13}\text{C}$ signatures of SOC regarding internal soil processes should be aligned with pollen records to ascertain or rule out the impacts of vegetation changes. The storage, translocation and isotopic signature of pyrogenic C, PhytOC, DOC and the necromass of several microbes (fungi, bacteria, archaea) should be further studied to improve modelling of C cycles and elucidate their importance in SOC stabilisation. The effects of roots on the amount of SOC and the $\delta^{13}\text{C}$ signature in the subsoil should be further evaluated in several recent ecosystems and on larger timescales (during whole pedogenesis). Future research should assess how fresh DOC from deep roots can cause priming effects on native SOC (Schiedung et al. 2023), potentially resulting in changes in the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures of the SOC. The cumulative small effects of the C recycling of different microbial communities on the isotopic signatures of SOC deserve further attention. New experiments should be designed to consider the internal and external drivers and processes affecting the $\delta^{13}\text{C}$ signatures of SOC separately.

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Declarations

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