Sciencexpress Report

Carbon Isotope Constraints on the Deglacial CO_2 Rise from Ice Cores

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The stable carbon isotope ratio of atmospheric CO_2 ($\delta^{13}C_{atm}$) is a key parameter to decipher past carbon cycle changes. Here we present $\delta^{13}C_{atm}$ data for the last 24,000 years derived from three Antarctic ice cores. We conclude that a pronounced 0.3‰ decrease in $\delta^{13}C_{atm}$ during the early deglaciation can be best explained by upwelling of old, carbon-enriched waters in the Southern Ocean. Later in the deglaciation, regrowth of the terrestrial biosphere, changes in sea surface temperature, and ocean circulation governed the $\delta^{13}C_{atm}$ evolution. During the Last Glacial Maximum, $\delta^{13}C_{atm}$ and CO_2 were essentially constant, suggesting that the carbon cycle was in dynamic equilibrium and that the net transfer of carbon to the deep ocean had occurred before then.

During the last 800,000 years (800 kyr), atmospheric CO_2 concentrations have varied in close relation to Antarctic temperatures (*1*, *2*) and the general waxing and waning of continental ice sheets. In particular, CO_2 rose from a stable level of 190 parts per million by volume (ppmv) during the Last Glacial Maximum to about 280 ppmv in preindustrial times, showing pronounced differences in atmospheric CO_2 rates of change in the course of the last glacial/interglacial transition (*3*). Many processes have been involved in attempts to explain these CO_2 variations, but it has become evident that none of these mechanisms alone can account for the 90 ppmv increase in atmospheric CO_2. A combination of processes must have been operating (*4*, *5*), with their exact timing being crucial. However, a unique solution to the deglacial carbon cycle changes has not been yet found.

In this respect, high-resolution and precise $\delta^{13}C_{atm}$ records from Antarctic ice cores are needed to better constrain the evolution of carbon cycle changes during the last deglaciation. On millennial time scales, $\delta^{13}C_{atm}$ is primarily influenced by the $\delta^{13}C$ of dissolved inorganic carbon (DIC) ($\delta^{13}C_{DIC}$) and sea surface temperature (SST), which controls the isotopic fractionation during air/sea gas exchange. The continuous rain of isotopically light organic material to the interior of the ocean draws down carbon from the surface layer to intermediate and deep waters, where the organic carbon is remineralized. Consequently, a vertical $\delta^{13}C_{DIC}$ gradient is established, controlled by the interplay of the ocean circulation with this so-called "biological pump". The more intense the circulation, the smaller the gradients are for $\delta^{13}C_{DIC}$, DIC, oxygen and nutrients. Superimposed on these marine carbon cycle processes are climate-induced changes in terrestrial biosphere carbon storage, which result in a net change in the carbon isotopic composition of the ocean/atmosphere system. On orbital time scales, weathering and sedimentation of $CaCO_3$ affect $\delta^{13}C_{DIC}$, $\delta^{13}C_{atm}$ and atmospheric CO_2 as well.

Until recently (*6*), analytical constraints represented the fundamental limitation on the utility of $\delta^{13}C_{atm}$ ice core records (*7*, *8*). Here we provide evidence (Fig. 1) about possible causes of carbon cycle changes with measurements of $\delta^{13}C_{atm}$ from two Antarctic ice cores (EPICA (European Project for Ice Coring in Antarctica) Dome C and Talos Dome), performed with three independent methods in two different labs (referred to as Bern sublimation, Bern cracker and Grenoble mill data) (*6*, *9*). One of our records is based on a sublimation method (*10*) that avoids the effects associated with incomplete gas extraction and thus yields more precise results (see Supporting Online Material (SOM)). A stringent residual analysis of the three data sets shows virtually no offset between the two Bern data sets and only a small systematic offset between the Bern and Grenoble data of 0.16‰, which can be explained by a method-dependent systematic fractionation. After correction of this offset, we combined the three $\delta^{13}C_{atm}$ records over the last 24 kyr using an error-weighted Monte Carlo bootstrap approach. This method showed that all three data sets are essentially compatible within their analytical uncertainties. To make full use of the resolution and precision of the data, the inclusion of all three data sets is required, although all our conclusions are also supported by the individual records. The final data set consists of 201 individual measurements, each reflecting typically 2 to 4 replicates and with an analytical 1σ error between 0.04 and 0.12‰. Since the resulting Monte Carlo Average (MCA) removes most of the analytical uncertainties, it contains less high-frequency variability compared to the raw data. This is in line with the centennial-scale low-pass filtering inherent to the bubble enclosure process at Dome C. Accordingly, the retained variability can be regarded as the signal most representative of millennial $\delta^{13}C_{atm}$ changes (see SOM for details regarding the MCA and its uncertainty).

Our $\delta^{13}C_{atm}$ data are in good agreement with previously published lower-resolution records (*6*, *9*). Our record shows a very stable level between 24 and ca. 19 kyr before present (BP, where present is defined as 1950), with an average $\delta^{13}C_{atm}$ of -6.45‰ (tables S1 and S2), similar to the -6.35‰ of the Late Holocene (Fig. 2B). Given the fact that a large set of environmental parameters such as atmospheric CO_2, global SST, terrestrial carbon storage, and ocean circulation have varied between the LGM and the Late Holocene, almost identical $\delta^{13}C_{atm}$ values indicate that opposing effects must have offset each other (*11*). This becomes clear if we look at three first-order effects on $\delta^{13}C_{atm}$: A SST rise of 1 K translates into a 0.1‰ increase in $\delta^{13}C_{atm}$, due to temperature-dependent fractionation between atmospheric CO_2 and marine DIC species (*12*). Assuming a global LGM-to-Holocene SST rise of 3 K would result in about 0.3‰ higher $\delta^{13}C_{atm}$ for the Holocene, provided that SST distribution and CO_2 gross flux exchange patterns remained constant. This effect is further augmented by the uptake of isotopically light carbon by the land biosphere and counterbalanced by the smaller vertical gradient in $\delta^{13}C_{DIC}$ in the Holocene ocean, supported by marine data (*13*). The fact that both $\delta^{13}C_{atm}$ and CO_2 show little variation from 24 to 19 kyr BP points to the carbon cycle being essentially in dynamic equilibrium at that time. As can also be seen in Fig. 2, the climate variations related to Heinrich stadial 2 (HS2) and Dansgaard-Oeschger event 2 (DO2) had little effect on the global carbon cycle during this time interval. Howev-

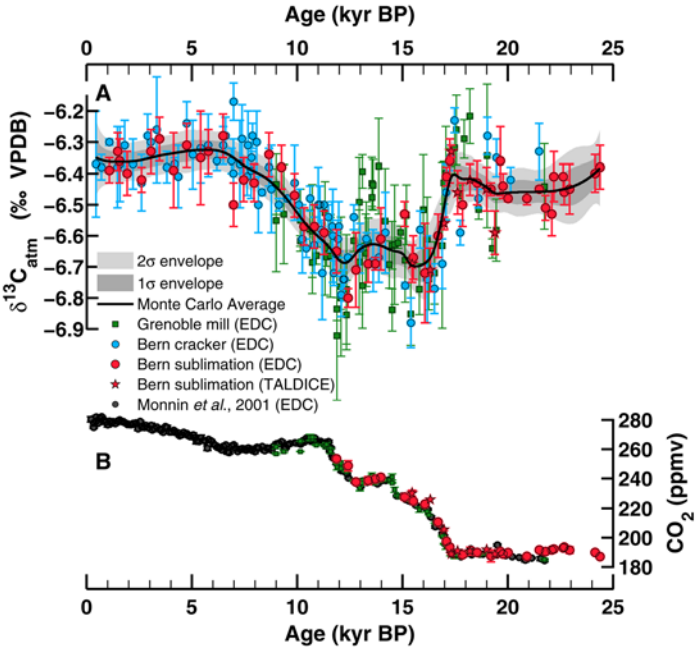


Fig. 1. Ice core reconstructions of atmospheric $\delta^{13}C$ and CO_2 concentration covering the last 24 kyr. (**A**) $\delta^{13}C_{atm}$ of atmospheric CO_2 measured with three different methods on two different ice core drill sites. Blue circles: Bern cracker data, green squares: Grenoble mill data (*9*) after offset correction, red circles: Bern sublimation data. Red stars indicate values from the sublimation method but measured on Talos Dome Ice Core (TALDICE). Error bars represent the standard deviation of replicate measurements. The black line is the result of 4000 Monte Carlo simulations representing an error-weighted average of the different $\delta^{13}C_{atm}$ data sets. The light and dark shaded areas represent the 2σ and 1σ error envelope around the Monte Carlo Average (see SI). (**B**) CO_2 concentration. Black circles represent earlier measurements on EDC (*3*), other symbols are the same as in panel **A**. Note: All ice core records are plotted on a synchronized age scale (*32*).

er, given the opposing trends for reconstructed atmospheric $\Delta^{14}C$ ($\Delta^{14}C_{atm}$) (*14*, *15*) and the expected $\Delta^{14}C_{atm}$ evolution (*16*) based on variations in ^{14}C production rate (*17*, *18*), the global ^{14}C budget was not balanced (Fig. 2A).

After a very small increase in $\delta^{13}C_{atm}$ at the very end of the glacial, a sharp drop in $\delta^{13}C_{atm}$ starting at 17.5 kyr parallels the onset of increasing atmospheric CO_2. Taken at face value, this would point to an early SST rise that preceded the onset of the CO_2 increase. When we apply a crude SST correction to our $\delta^{13}C_{atm}$ databased on a global estimate of SST temperature changes during the transition (see SOM), this $\delta^{13}C_{atm}$ increase vanishes (Fig. 2B). Note, however, that this 0.06‰ excursion is within the uncertainties of our data and that other effects could also lead to this small enrichment in $\delta^{13}C_{atm}$. The 0.3‰ drop in $\delta^{13}C_{atm}$ after the onset of the transition at 17.5 kyr BP is accompanied by a CO_2 increase of about 35 ppmv and a 190‰ drop in $\Delta^{14}C_{atm}$ (*19*), which has been attributed to a release of old carbon from the deep ocean. This coeval drop in $\delta^{13}C_{atm}$ and $\Delta^{14}C_{atm}$ during the so-called "mystery interval", 17.5 – 14 kyr BP (*19*), is arguably the most enigmatic carbon cycle change in the course of the transition and will be discussed in more detail below.

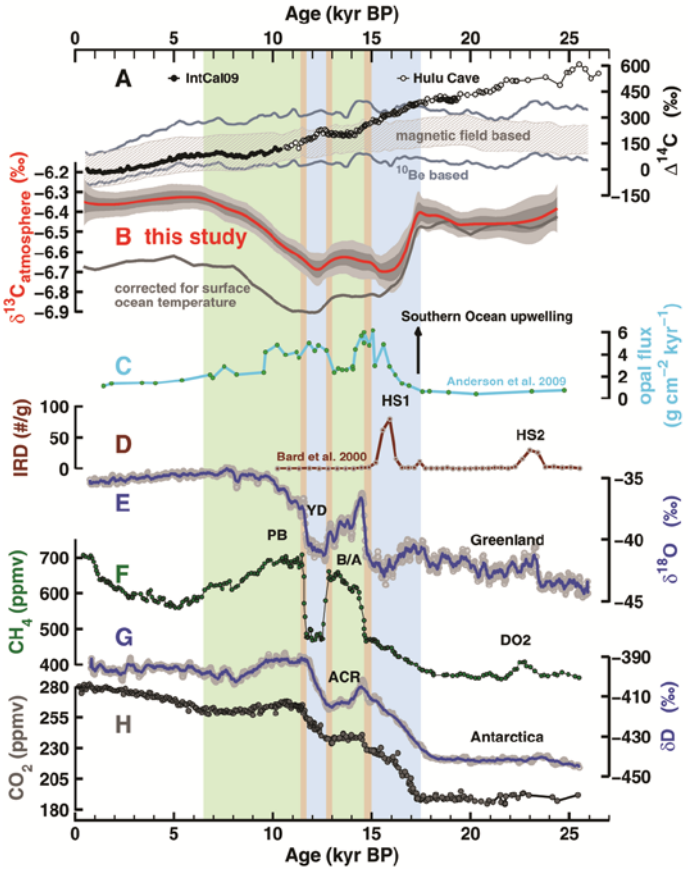
After the broad $\delta^{13}C_{atm}$ minimum is reached at about 16 kyr BP, $\delta^{13}C_{atm}$ increases slightly by 0.1‰ during the pronounced Bølling-Allerød (BA) warming. Other than circulation changes in the Southern Ocean (*20*), the regrowth of the terrestrial biosphere in the northern hemisphere could contribute to this increase in $\delta^{13}C_{atm}$ (*4*). However, since the SST-corrected $\delta^{13}C$ evolution (Fig. 2B) does not show any increase, a robust process attribution requires precisely dated SST reconstructions and transient carbon cycle modeling.

An almost linear rise by 0.06‰ per kyr follows the second $\delta^{13}C_{atm}$ minimum at 12.2 kyr BP, leading to maximum values of -6.33‰ at around 6 kyr BP. This rise might be largely explained by the continuing regrowth of the terrestrial biosphere (*21*), in concert with smaller contributions from SST warming and changes in circulation and export production (*9*, *22*). From this mid-Holocene maximum, $\delta^{13}C_{atm}$ values decline slightly to reach values of -6.35‰ at 0.5 kyr BP, as previously reported (*6*).

As mentioned above, the carbon cycle changes during the mystery interval have been a matter of intense debate (*19*, *20*, *23*). Our high-resolution $\delta^{13}C_{atm}$ record together with other records of carbon cycle changes and insights from models may help to constrain hypotheses put forward to explain the mystery interval. The rise in CO_2 and the decline in $\delta^{13}C_{atm}$ and $\Delta^{14}C_{atm}$ between 17 and 15 kyr BP fit the concept of bringing DIC-rich waters with old carbon into exchange with the atmosphere. Indicative ^{14}C signals of upwelling of old, CO_2-enriched deep water were found in Pacific intermediate waters (*24*), but others (*23*) ruled out such old water in the northeast Pacific, and evidence for a ^{14}C-depleted glacial deep ocean remains elusive (*19*, *23*, *25*). These $\Delta^{14}C$ studies were usually confronted with variable reservoir age between benthic and planktonic foraminifera. A study using deep sea corals now circumvents this problem by applying absolute U-Th dating and shows that the deep glacial Southern Ocean indeed ventilated its ^{14}C-depleted reservoir during the mystery interval (*26*).

The constant $\delta^{13}C_{atm}$ values during the late glacial indicate that the build-up of such an old, DIC-rich reservoir must have occurred before 24 kyr BP. A large number of records mark the start of the deglaciation around 17 kyr BP (Fig. 2). Within the uncertainty in marine and ice core age scales, the CO_2 increase, the pronounced $\Delta^{14}C_{atm}$ drop (*15*), the resumption of vigorous Southern Ocean upwelling as recorded in intense deposition of biogenic opal (*20*), and the launch of ice-rafted debris layers at the beginning of the Heinrich 1 stadial (*27*) all occurred simultaneously. Interestingly, our $\delta^{13}C_{atm}$ record shows its largest deviation of 0.3‰, i.e., the entire $\delta^{13}C_{atm}$ decrease from the LGM to the Preboreal (PB), within the first 2 kyr after the start of the deglaciation. Within the same interval, CO_2 rose by 30 ppmv from 190 ppmv to 220 ppmv, i.e., only 35% of the LGM-PB rise. Together with the trend reversal in $\delta^{13}C_{atm}$ toward the end of the mystery interval, this indicates that only a fraction of the glacial/interglacial CO_2 increase can be explained by an intensification of deep ocean ventilation bringing isotopically depleted and carbon-rich water to the surface of the Southern Ocean. Our new, high-resolution $\delta^{13}C_{atm}$ data constrain the period of this release of isotopically depleted carbon from the deep ocean to the atmosphere to between 17.4 kyr BP and 15 kyr BP. This interpretation of the proxy records is quantitatively in line with dynamical ocean model results that link deep ocean ventilation, atmospheric CO_2, $\delta^{13}C_{atm}$, $\delta^{13}C_{DIC}$, opal burial, and radiocarbon (*28*).

Alternative hypotheses (*29*, *30*) invoking the release of old carbon from permafrost or carbon locked under continental ice sheets are unlikely to explain the carbon cycle changes in the mystery interval because the amount of terrestrial carbon needed to account for the ^{14}C drop is very large, at 5000 Gt (*25*), and would conflict with the moderate 30 ppmv rise in atmospheric CO_2. Moreover, it would lead to an overall decline in $\delta^{13}C_{DIC}$, which is not observed in benthic foraminifera in the deep ocean (*13*, *22*). Also, a carbonate dissolution event at the sea floor that would have to accompany such a large terrestrial carbon release into the atmosphere/ocean system is not imprinted in the deglacial marine



$CaCO_3$ record (*31*)

Consequently, despite the fact that the search for an extremely ^{14}C-depleted deep water mass in marine records has thus far not been successful (*23*) and might not even essential to explain the $\Delta^{14}C_{atm}$ anomaly (*26*), the release of carbon from the deep ocean remains the most plausible scenario to explain the early deglacial drop in our new $\delta^{13}C_{atm}$ record. Furthermore, model results suggest that a $\delta^{13}C_{atm}$ decrease of 0.3‰ and a CO_2 increase of about 30 ppmv can be accommodated by relatively small (about 20‰) and spatially complex changes in deep ocean $\Delta^{14}C$ (*28*). These changes may remain undetected in the search for the old abyssal water using benthic foraminifera (*19*, *25*). However, they are also too small to explain the reconstructed $\Delta^{14}C_{atm}$ decline in the mystery interval. Based on these considerations, the currently available marine and ice core information cannot be reconciled with the atmospheric radiocarbon record in a straightforward manner. One possibility to resolve this issue is to also reconsider a larger change in ^{14}C production between the Holocene and the glacial, and to work toward independent verification of the $\Delta^{14}C_{atm}$ history.

Fig. 2. Ice core reconstructions and marine records illustrating the evolution of major components of the Earth climate system over the last 24 kyr. (**A**) Reconstructed $\Delta^{14}C_{atm}$ from IntCal09 (*14*) and the ^{230}Th-dated Hulu Cave $\Delta^{14}C_{atm}$ record (*15*) compared with modeled (*16*) $\Delta^{14}C_{atm}$ assuming a constant carbon cycle under pre-industrial conditions but considering temporal changes in ^{14}C production (either based on ^{10}Be (*18*), upper and lower estimates enveloped in gray lines, or on paleomagnetic field intensity (*17*), hatched area). (**B**) Monte Carlo simulations (this study) of the evolution of $\delta^{13}C_{atm}$ before (red line represents the MCA, 2σ and 1σ envelopes are in gray) and after SST correction (gray line; see SI) (**C**) Opal flux in the Southern Ocean as a proxy for local upwelling (*20*). (**D**) Record of ice rafted debris (IRD) in the North Atlantic associated with Heinrich stadials (HS1 and HS2) (*27*). (**E**) Greenland temperature proxy $\delta^{18}O$ (*33*). (**F**) Reconstructed atmospheric CH_4 concentration (*34*) (**G**) Antarctic temperature proxy δD from the EDC ice core (*35*). (**H**) Compilation of reconstructed CO_2 shown in Fig. 1B. Green bars indicate intervals with a strong net terrestrial carbon build-up, blue bars indicate intervals where sequestered deep ocean CO_2 was released back to the atmosphere. Note: Ice core records are plotted on a synchronized age scale (*32*), other records are plotted on their individual age scales.

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Acknowledgments: We thank two anonymous reviewers for carefully reviewing the manuscript. Financial support for this study was provided in part by Deutsche Forschungsgemeinschaft (DFG), Helmholtz Gemeinschaft, and Schweizerischer Nationalfonds (SNF). This work is a contribution to the "European Project for Ice Coring in Antarctica" (EPICA), a joint European Science Foundation/European Commission (EC) scientific program, funded by the EC under the Environment and Climate Program and by national contributions from Belgium, Denmark, France, Germany, Italy, The Netherlands, Norway, Sweden, Switzerland, and UK The main logistic support at Dome C was provided by the Institut Polaire Français – Paul Emile Victor (IPEV) and PNRA. Ice core material was also used from the Talos Dome Ice Core Project (TALDICE), a joint European program led by Italy and funded by national contributions from Italy, France, Germany, Switzerland and the UK. The main logistical support at Talos Dome was provided by PNRA. This is EPICA publication No. 284. The data are accessible online at http://doi:10.1594/PANGAEA.772713.

Supplementary Materials
www.sciencemag.org/cgi/content/full/science.1217161/DC1
Materials and Methods
Figs. S1 to S7
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28 November 2011; accepted 19 March 2012

Published online 29 March 2012; 10.1126/science.1217161
10.1126/science.1217161

Sciencexpress Perspective

CLIMATE CHANGE

The Ice Age Carbon Puzzle

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A carbon isotope record helps to explain why carbon dioxide concentrations change during ice age cycles.

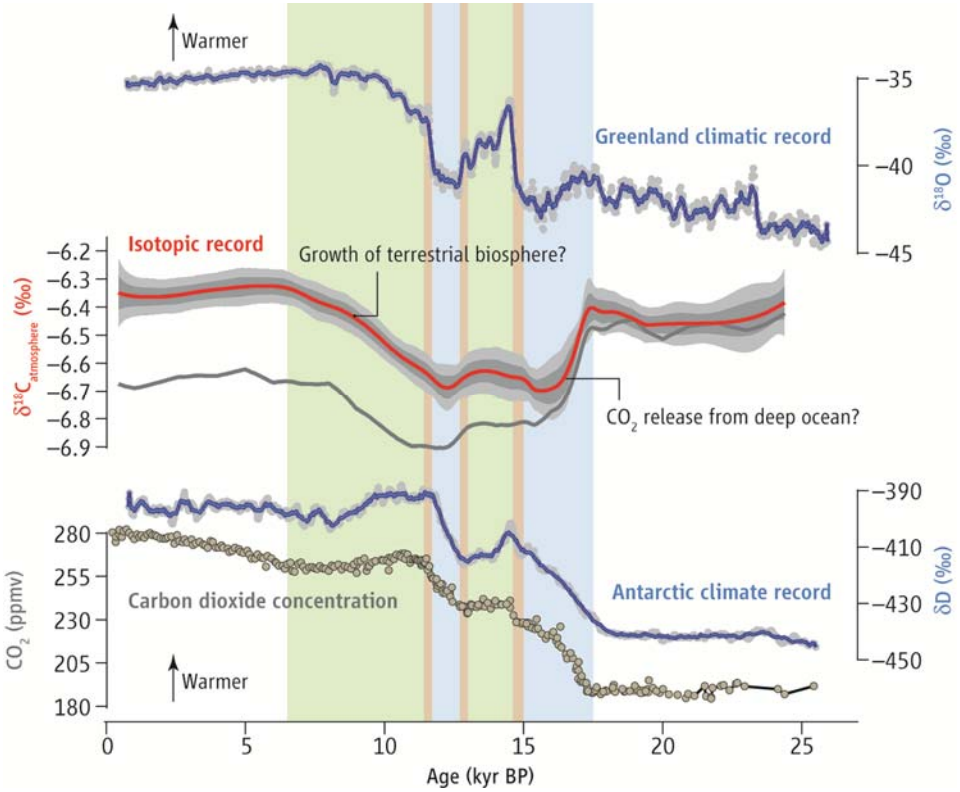
Between about 24,000 years ago and today, the large ice sheets covering most of Canada and parts of Europe and Asia melted away, sea level rose by 120 m, Earth warmed by about 5°C, and rainfall and vegetation patterns shifted, sometimes abruptly. This dramatic natural climate experiment was set in motion by cyclic variations in the geometry of Earth's orbit, but a complex system of feedbacks governed the transition from a glacial to an interglacial state. One of the most important of these feedbacks was a well-documented change in the atmospheric greenhouse gas carbon dioxide (CO_2) (*1*). In this week's *Science* Express, Schmitt *et al*. (*2*) provide important new carbon isotopic data that help to explain these changes.

Multiple studies of air trapped in polar ice have shown that ~17,500 years ago CO_2 levels started to rise from ice age levels of about 180 parts per million (ppm), reaching about 265 ppm 10,000 years ago (see the figure). Over the next 10,000 years, CO_2 slowly rose by another 20 ppm, until the rapid increase that started in the industrial age took over. Looking farther back in time, CO_2 variations appear to be a fundamental characteristic of ice age cycles (*3*).

Exactly why CO_2 changed like this has been vexing geochemists for decades. The carbon cycle involves uptake and release of CO_2 from both land and oceanic reservoirs, and these processes operate on many time scales. No one unified theory fits all available evidence, nor is the available evidence sufficient to test all hypotheses. The stable carbon isotopic composition of CO_2 could help to resolve these issues. This is because various carbon cycle processes fractionate the heavy isotope ^{13}C from the lighter ^{12}C. Photosynthesis, for example, preferentially removes ^{12}C from the atmosphere, and isotope fractionation during inorganic partitioning of CO_2 between the atmosphere and ocean are also important. However, apart from the clear isotopic signature of fossil fuel CO_2 input since the industrial revolution (*4*), and some hints from pioneering work (*5*, *6*), ice core isotopic measurements have not been detailed or precise enough to yield consistent patterns. Schmitt *et al*. now move the isotopic story forward with an important data set.

The primary problems to overcome have been technical. Available ice samples tend to be small, and the isotopic variations are also relatively small, making it both difficult and necessary to make precise measurements. Extracting air for CO_2 measurements requires either mechanical disaggregation or sublimation under vacuum, plus purification of CO_2, all of which can introduce artifacts. Furthermore, at deeper depths in the great ice sheets, air slowly changes from being occluded in bubbles to a solid hydrate form. Releasing air from hydrates by mechanical means is inefficient, and fractionation between bubbles and hydrates can cause further problems.

Schmitt *et al*. have overcome some of these challenges to produce the best record to date of the glacial to interglacial variations in stable carbon isotopes of CO_2. They adapted and painstakingly refined a tradi-



Glacial-interglacial change. Over the course of the past 24,000 years, CO_2 concentrations have risen (black curve) (*1*) as Earth emerged from glaciation, as shown by climate records from Greenland and Antarctica (blue curves) (*14*, *15*). Schmitt *et al*. (*2*) report a record of the change in the $^{13}C/^{12}C$ ratio of CO_2 during this time (red curve). The isotopic ratio is expressed in delta notation, where $\delta^{13}C$ is the deviation of a sample ratio from that of an internationally expected standard, expressed in parts per thousand. Comparison of the CO_2 record with the isotopic record provides insights into the mechanisms behind the CO_2 rise.

tionally cumbersome technique of sublimating ice, and coupled it with a sensitive mass spectrometric technique to measure isotope ratios (*7*). Schmitt *et al*. augmented their latest sublimation data set with several others, although the results are primarily drawn from one Antarctic ice core. To create a unified picture of isotopic variations for the past 24,000 years, they smoothed the combined record using a method that incorporates analytical uncertainty. The resulting curve provides a good picture of isotopic variations on thousand-year time scales, at the expense of losing resolution of more detailed variations.

The data provide much food for thought. Going forward in time from 24,000 years ago, the isotopic pattern resembles a somewhat distorted letter W. The first event is a rapid 0.3 per mil depletion in ^{13}C between about 17,500 and 14,000 years, a time when the CO_2 concentration rose by about 60 ppm. Schmitt *et al*. suggest that this is consistent with release of CO2 from a previously isolated deep-ocean reservoir that accumulated carbon due to oxidation of organic detritus sinking from the surface ocean. Variants of this hypothesis have been presented recently (*8*, *9*), and the idea gains support from the fact that the amount of radioactive ^{14}C in the atmosphere dropped drastically at about the same time as the carbon isotope ratio decreased (*10*). Studies of ^{14}C in fossil organisms found in deep sea sediments, which can provide estimates of the age of ancient deep ocean water, both support (*11*, *12*) and call into question (*13*) the existence and ventilation of the isolated reservoir.

The middle section of the W, between about 14,000 and 12,000 years ago, is subdued (see the figure). There are hints of variations that may be related to abrupt climate change seen in ice cores and other records, but they are too small to be interpreted clearly. This interval contains most of the remaining glacial-interglacial change in CO_2, and the lack of major isotopic change may indicate a different mechanism for this change than for the previous increase.

The other end of the W-shaped pattern is a slow rise in the isotope ratio between about 12,000 and 7000 years ago. Schmitt *et al*. suggest that this increase may reflect growth of the terrestrial biosphere, which preferentially removes ^{12}C from the atmosphere.

Schmitt *et al*. provide plausible interpretations of their results, but the role of other processes—including the input of magmatic CO_2 and the release of carbon from the terrestrial biosphere, among others—remain to be fully evaluated. Large-scale carbon cycle models will be needed to explore the full significance of these long-awaited data.

One limitation of the results is that the smoothed record does not allow us to see more rapid changes in the isotopic ratio of CO_2. Such changes are possible and could provide important clues to why so many of the inflection points during the glacial-interglacial CO_2 rise seem to correspond to abrupt shifts in climate seen in ice cores in Greenland and Antarctica (see the figure).

Schmitt *et al*. have paved the way for more laborious lab work that may further unwrap these and other mysteries, and ultimately lead to a more complete understanding of carbon cycle feedbacks. Such feedbacks will operate during the current human experiment with the climate system, and therefore are important to understand.

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Published online 29 March 2012
10.1126/science.1219710