A Pleistocene ice core record of atmospheric O2 concentrations

D. Stolper, M. Bender, G. Dreyfus, Y. Yan, J. Higgins

deliver westward acceleration to the mean flow. Furthermore, the stronger tropical upwelling during Boreal winter slows down the QBO's descent, allowing more time for the extratropical waves to impact during this particular phase.

Of course, it is also possible that our current numerical models can not properly represent the processes disrupting the QBO. To investigate this, the foregoing RMS analysis that was applied to the observational record was applied to historical global climate model runs so as to identify possible analogous events (Fig. 4, A to C). Among the available models that produce a QBO internally, only one rarely produced behavior similar to the observed disruption, with an example shown in Fig. 4D. The extreme profiles resemble those observed during 2016 with a thin layer of westward wind appearing within an otherwise eastward QBO phase.

What will happen next? The recent disruption of the QBO is a rare event that occurs in the northern winter. The forecast initialized after the disruption (Fig. 3B) suggests that the QBO will return to more regular phase progression over the coming year. The westward jet that suddenly appeared in the lower stratosphere is predicted to amplify in the summer of 2016 and progress downward with time. Eastward flow then descends from the 20-hPa level and dominates the lower stratospheric flow toward the end of 2016, returning the QBO to its typical behavior. We then expect regular and predictable QBO cycling to continue from 2017, as occurs in the available climate models (Fig. 4D). Nonetheless, as the climate warms in the future, climate models that simulate these events suggest that similar disruptions will occur up to three times every 100 years for the more extreme of the standard climate change scenarios. This is consistent with a projected strengthening of the Brewer-Dobson circulation due to increasing stratospheric wave activity (*14*) and the recently observed weakening of the QBO amplitude in the lower stratosphere (*21*) under climate change. However, robustly modeling how the QBO and its underlying processes and external influences will change in the future remains elusive.

There is a further outcome of the 2016 disruption of the QBO. After an eastward QBO at the onset of the 2015–2016 winter, the QBO at the onset of the coming winter of 2016–2017 was expected to be westward. The disruption of early 2016 means that an eastward QBO phase is now again expected in the lower stratosphere. Because of the expected QBO influence on the Atlantic jet stream, this increases the risk of a strong jet, winter storms, and heavy rainfall over northern Europe in the coming winter (*22*, *23*).

Note added in proof: A similar finding was published by Newman *et al.* (*24*) during the final revision period of the present study.

REFERENCES AND NOTES

1. R. A. Ebdon, *Q. J. R. Meteorol. Soc.* **86**, 540–542 (1960).
2. R. J. Reed, W. J. Campbell, L. A. Rasmussen, D. G. Rogers, *J. Geophys. Res.* **66**, 813–818 (1961).
3. M. P. Baldwin *et al.*, *Rev. Geophys.* **39**, 179–229 (2001).
4. J. M. Wallace, *Rev. Geophys.* **11**, 191 (1973).
5. P. H. Haynes, *Q. J. R. Meteorol. Soc.* **124**, 2645–2670 (1998).
6. U. Niemeier *et al.*, *Atmos. Chem. Phys.* **9**, 9043–9057 (2009).
7. J. R. Holton, H.-C. Tan, *J. Atmos. Sci.* **37**, 2200–2208 (1980).
8. J. A. Anstey, T. G. Shepherd, *Q. J. R. Meteorol. Soc.* **140**, 1–21 (2014).
9. J. Kidston *et al.*, *Nat. Geosci.* **8**, 433–440 (2015).
10. A. A. Scaife *et al.*, *Geophys. Res. Lett.* **41**, 1752–1758 (2014).
11. B. Naujokat, *J. Atmos. Sci.* **43**, 1873–1877 (1986).
12. R. S. Lindzen, J. R. Holton, *J. Atmos. Sci.* **25**, 1095–1107 (1968).
13. J. R. Holton, R. S. Lindzen, *J. Atmos. Sci.* **29**, 1076–1080(1972).
14. N. Butchart, *Rev. Geophys.* **52**, 157–184 (2014).
15. A. R. Plumb, R. C. Bell, *Q. J. R. Meteorol. Soc.* **108**, 335–352 (1982).
16. R. E. Dickinson, *J. Atmos. Sci.* **25**, 984–1002 (1968).
17. T. J. Dunkerton, *Atmos.-Ocean* **21**, 55–68 (1983).
18. K. Hamilton, A. Hertzog, F. Vial, G. Stenchikov, *J. Atmos. Sci.* **61**, 383–402 (2004).
19. J. S. Kinnersley, S. Pawson, *J. Atmos. Sci.* **53**, 1937–1949 (1996).
20. C. MacLachlan *et al.*, *Q. J. R. Meteorol. Soc.* **141**, 1072–1084 (2015).
21. Y. Kawatani, K. Hamilton, *Nature* **497**, 478–481 (2013).
22. R. A. Ebdon, *Aust. Meteorol. Mag.* **104**, 282–285 (1975).
23. C. Huntingford *et al.*, *Nat. Clim. Change* **4**, 769–777 (2014).
24. P. A. Newman, L. Coy, S. Pawson, L. R. Lait, *Geophys. Res. Lett.* 10.1002/2016GL070373 (2016).
25. D. P. Dee *et al.*, *Q. J. R. Meteorol. Soc.* **137**, 553–597 (2011).
26. D. G. Andrews, M. E. McIntyre, *J. Atmos. Sci.* **33**, 2031–2048 (1976).
27. NCAS British Atmospheric Data Centre, European Centre for Medium-Range Weather Forecasts: ECMWF operational analysis: Assimilated Data (2006); http://catalogue.ceda.ac.uk/uuid/c46248046f6ce34fc7660a36d9b10a71.
28. E. P. Gerber *et al.*, *Bull. Am. Meteorol. Soc.* **93**, 845–859 (2012).

ACKNOWLEDGMENTS

We thank the European Centre for Medium-Range Weather Forecasts for providing ERA-Interim and Operational Analysis data (www.ecmwf.int/en/forecasts) and the Freie Universität Berlin for providing radiosonde data (www.geo.fu-berlin.de/en/met/ag/strat/produkte/qbo). The CMIP5 data was obtained from the British Atmospheric Data Centre (browse.ceda.ac.uk/browse/badc/cmip5). A summary of data used in the study is listed in table S1. S.M.O. was supported by UK Natural Environment Research Council grants NE/M005828/1 and NE/P006779/1. A.A.S., J.R.K., and N.B. were supported by the Joint UK Business, Energy and Industrial Strategy/Defra Met Office Hadley Centre Climate Programme (GA01101). A.A.S. and J.R.K. were additionally supported by the EU Seventh Framework Programme SPECS (Seasonal-to-decadal climate Prediction for the improvement of European Climate Services) project. We acknowledge the scientific guidance of the World Climate Research Programme for helping motivate this work, coordinated under the framework of the Stratosphere-troposphere Processes and their Role in Climate (SPARC) QBOi activity led by S.M.O., J.A.A., N.B., and K.H. The analysis of observations and reanalyses was performed by K.H., C.Z., S.M.O., J.A.A., and N.B. J.R.K. and A.A.S. provided the analysis of the seasonal forecasts, and V.S. identified analogous events in global climate model output. A.A.S. first alerted us to the disruption of the QBO in observational data. All authors were equally involved in the interpretation of the results and preparation of the manuscript.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/353/6306/1424/suppl/DC1
Table S1

2 July 2016; accepted 29 August 2016
10.1126/science.aah4156

ATMOSPHERIC OXYGEN

A Pleistocene ice core record of atmospheric O_2 concentrations

D. A. Stolper,[1]* M. L. Bender,[1,2] G. B. Dreyfus,[1,3]† Y. Yan,[1] J. A. Higgins[1]

The history of atmospheric O_2 partial pressures (P_{O_2}) is inextricably linked to the coevolution of life and Earth's biogeochemical cycles. Reconstructions of past P_{O_2} rely on models and proxies but often markedly disagree. We present a record of P_{O_2} reconstructed using O_2/N_2 ratios from ancient air trapped in ice. This record indicates that P_{O_2} declined by 7 per mil (0.7%) over the past 800,000 years, requiring that O_2 sinks were ~2% larger than sources. This decline is consistent with changes in burial and weathering fluxes of organic carbon and pyrite driven by either Neogene cooling or increasing Pleistocene erosion rates. The 800,000-year record of steady average carbon dioxide partial pressures (P_{CO_2}) but declining P_{O_2} provides distinctive evidence that a silicate weathering feedback stabilizes P_{CO_2} on million-year time scales.

The importance of O_2 to biological and geochemical processes has led to a long-standing interest in reconstructing past atmospheric O_2 partial pressures (P_{O_2}, reported at standard temperature and pressure) (*1*–*12*). However, there is no consensus on the history of Phanerozoic P_{O_2}, with reconstructions disagreeing by as much as 0.2 atm, the present-day pressure of O_2 in the atmosphere (e.g., *7*, *10*). Even over the past million years, it is not known whether atmospheric O_2 concentrations varied or whether the O_2 cycle was in steady state (Fig. 1A). Knowledge of P_{O_2} over the past million years could provide new insights into the O_2 cycle on geologic time scales and serve as a test for models and proxies of past P_{O_2}. Here we present a primary record of P_{O_2} over the past 800,000 years, reconstructed using measured O_2/N_2 ratios of ancient air trapped in polar ice.

O_2/N_2 ratios of this kind have been extensively used to date ice cores on the basis of the correlation between O_2/N_2 and local summertime

[1]Department of Geosciences, Princeton University, Princeton, NJ 08544, USA. [2]Institute of Oceanology, Shanghai Jiao Tong University, Shanghai 200240, China. [3]Laboratoire des Sciences du Climat et de l'Environnement, Gif-sur-Yvettte, France.
***Corresponding author. Email: dstolper@princeton.edu**
†Present address: U.S. Department of Energy, Washington, DC 20585, USA.

insolation (*13–17*). Despite being directly tied to atmospheric compositions, O_2/N_2 ratios have never before been used to reconstruct past P_{O_2}. Landais *et al.* (*16*) and Bazin *et al.* (*17*), while using O_2/N_2 ratios for ice core dating, noted a decline in O_2/N_2 values with time (i.e., toward the present). They suggested that this decline could be due to secular changes in air entrapment processes, gas loss during core storage, or changes in atmospheric O_2/N_2, but they did not evaluate these hypotheses. Given the potential for O_2/N_2 ratios to directly constrain Pleistocene P_{O_2}, we present compiled O_2/N_2 measurements from multiple ice core records and evaluate their geochemical implications.

We compiled published O_2/N_2 ice core records from Greenland [Greenland Ice Sheet Project 2 (GISP2) (*18*)] and Antarctica [Vostok (*13*), Dome F (*14*), and Dome C (*17*); table S1], along with previously unpublished Antarctic Ar/N_2 records [Vostok and Dome C; table S2]. The data were treated as follows [see (*19*) for more details]. (i) Measured ratios were corrected for gravitational fractionations and are reported using δ notation

$$\delta O_2/N_2 = 1000\times\left(\frac{[O_2]/[N_2]_{\text{sample}}}{[O_2]/[N_2]_{\text{preanthropogenic atmosphere}}}-1\right) \quad (1)$$

$$\delta Ar/N_2 = 1000\times\left(\frac{[Ar]/[N_2]_{\text{sample}}}{[Ar]/[N_2]_{\text{modern atmosphere}}}-1\right) \quad (2)$$

where brackets denote concentrations. A decrease in $\delta O_2/N_2$ of 1 per mil (‰) equates to a 0.1% decrease in P_{O_2} relative to the preanthropogenic atmosphere (i.e., the modern atmosphere corrected for fossil fuel combustion). We define the preanthropogenic atmosphere as having $\delta O_2/N_2$ = 0‰ and $\delta Ar/N_2$ = 0‰. (ii) Only analyses of bubble-free ice with clathrates were considered. (iii) The portions of the $\delta O_2/N_2$ and $\delta Ar/N_2$ signals linked to insolation (*13–17*) were removed (figs. S1 and S2). (iv) We corrected for differences in bubble close-off fractionations between ice cores and interlaboratory offsets by assuming that, in the absence of such effects, trapped gases of a given age share identical atmospheric O_2/N_2 and Ar/N_2 values (figs. S3 and S4).

The fully corrected data are plotted versus ice age in Figs. 1B ($\delta O_2/N_2$) and 2A ($\delta Ar/N_2$). $\delta O_2/N_2$ values decrease by 8.4‰ per million years (±0.2, 1σ), consistent with the observations of Landais *et al.* (*16*) and Bazin *et al.* (*17*). $\delta Ar/N_2$ values increase by 1.6‰ per million years (±0.2, 1σ), which is discussed below.

The decline in $\delta O_2/N_2$ with time could result from temporal changes in bubble entrapment processes, effects of ice core storage, a decline in P_{O_2}, or an increase in the partial pressure of atmospheric N_2 (P_{N_2}). We now evaluate these possibilities in the context of the $\delta O_2/N_2$ record.

$\delta O_2/N_2$ values of gas extracted from ice are ~5 to 10‰ lower than those of ambient air (*13–18, 20, 21*). Additionally, $\delta Ar/N_2$ covaries with $\delta O_2/N_2$ along slopes of 0.3 to 0.6 (fig. S5) (*19, 21, 22*). These depletions and covariations have been attributed to fractionations created during bubble close-off on the basis of measurements and models of firn air (*20, 22*) and the covariation of $\delta O_2/N_2$ and $\delta Ar/N_2$ with local insolation (figs. S1 and S2) (*13–17, 19*). If secular changes in bubble close-off fractionations caused the decline in $\delta O_2/N_2$, then $\delta Ar/N_2$ values should covary with $\delta O_2/N_2$ along slopes of 0.3 to 0.6 and thus decline by 2.5 to 5.0‰ per million years. Instead, $\delta Ar/N_2$ increases with time by 1.6‰ per million years (±0.2, 1σ; Fig. 2A). The increasing trend is largely due to a subset of Vostok data from 330,000- to 370,000-year-old ice that is lower in $\delta Ar/N_2$ by ~1‰ compared with younger data. Exclusion of this subset yields an increase in $\delta Ar/N_2$ with time of only 0.35‰ (±0.20, 1σ), within the 2σ error range of no change. Regardless, whichever way the $\delta Ar/N_2$ are analyzed, they are inconsistent with the decline in $\delta O_2/N_2$ being caused by bubble close-off processes (Fig. 2A).

Ice core storage, under some conditions, causes the $\delta O_2/N_2$ values of trapped gases to decline (*14–17*). Thus, the second possibility that we consider is that ice core storage lowered the $\delta O_2/N_2$ values so that the slope observed in Fig. 1 is an artifact. For example, a change in $\delta O_2/N_2$ correlated with ice age but unrelated to atmospheric compositions could result if the retention of O_2 versus N_2 during storage is a function of precoring properties controlled by original ice depths (e.g., in situ temperature, pressure, or clathrate size). We evaluate this possibility by using three approaches. (i) Gas loss during core storage causes $\delta Ar/N_2$ to decline at half the rate of $\delta O_2/N_2$ (*21, 23, 24*). However, as discussed above, the $\delta Ar/N_2$ values are not consistent with such a change (Fig. 2A). (ii) Because some ice properties (e.g., temperature and pressure) can vary linearly with ice depth, we tested whether the Dome C $\delta O_2/N_2$ data are better fit by a linear relationship when plotted against ice age or depth. We note that only the Dome C ice core's age-depth relationship is sufficiently curvilinear for this test to be useful. We linearly regressed both age and depth against

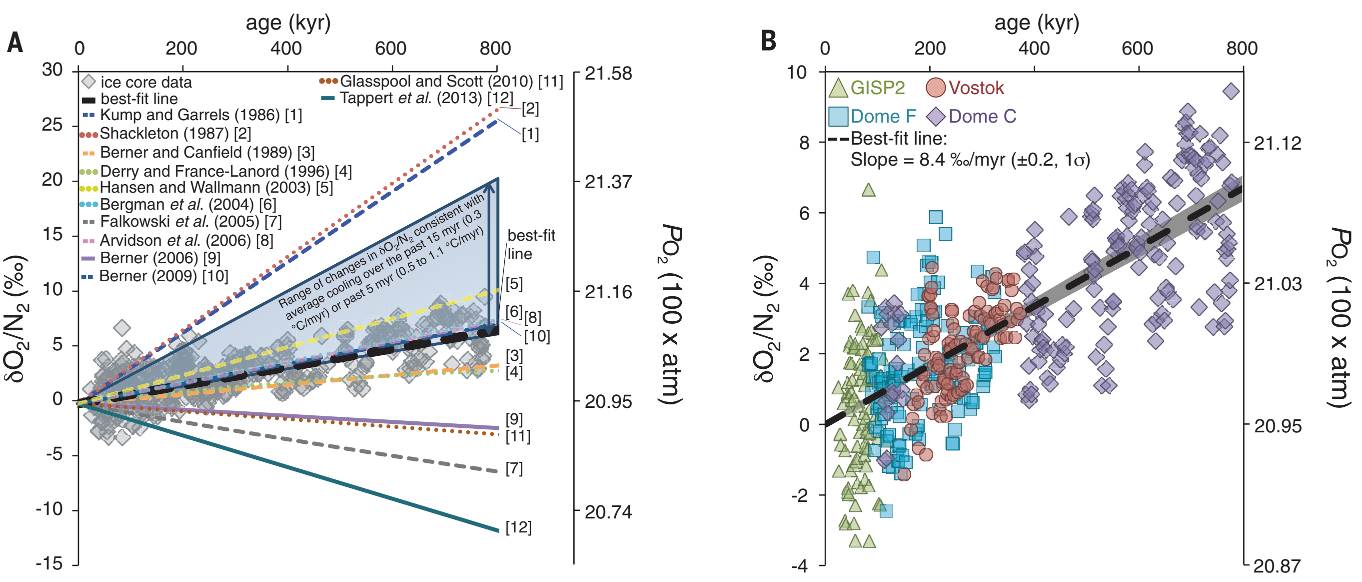

Fig. 1. $\delta O_2/N_2$ and P_{O_2} values versus age from ice cores and from model and proxy predictions. (**A**) Comparison of the ice core data with model and proxy predictions (*1–12*). (**B**) $\delta O_2/N_2$ versus ice age from ice cores. $\delta O_2/N_2$ decreases by 8.4‰ per million years (±0.2, 1σ). Gray bands are 95% confidence intervals. Data are corrected for gravitational, interlaboratory, and bubble close-off fractionations (*19*). kyr, thousand years; myr, million years.

$\delta O_2/N_2$ for ice older than ~400,000 years (i.e., deeper than 2600 m) and extrapolated the fits to younger ages and shallower depths. The extrapolation for age (Fig. 2B) passes through the younger data, whereas the extrapolation for depth (Fig. 2C) misses the shallower data (by >4σ). (iii) Repeat $\delta O_2/N_2$ measurements of Vostok ice from the same age interval (150,000 to 450,000 years ago) made 10 years apart (*13*, *15*) differ on average by 6‰, with longer storage leading to lower $\delta O_2/N_2$. Despite this, regressing $\delta O_2/N_2$ against time yields statistically identical (within 1σ) slopes of $\delta O_2/N_2$ versus age for both data sets (fig. S6).

Collectively, the data and tests presented above provide no support for the observed decrease in $\delta O_2/N_2$ over time being an artifact of either bubble close-off processes as they are currently understood or ice core storage. Consequently, we hypothesize and proceed with the interpretation that the observed decline in $\delta O_2/N_2$ reflects changes in P_{O_2} or P_{N_2}. Because N_2 has a billion-year atmospheric lifetime (*25*), we link the decline in $\delta O_2/N_2$ with time exclusively to a decline in P_{O_2}. Our hypothesis is further supported by the observation that data from all four ice cores individually exhibit the same general trends and magnitudes of decreasing $\delta O_2/N_2$ with time (table S3), even though each was drilled, stored, and analyzed differently.

The question raised by this record is why P_{O_2} has decreased by ~7‰ over the past 800,000 years. Changes in P_{O_2} require imbalances between O_2 sources [dominantly modern sedimentary organic carbon (C_{org}) and pyrite burial] and sinks (dominantly ancient sedimentary C_{org} and pyrite oxidation) (*26*). Thus, a higher rate of oxidative weathering relative to C_{org} and/or pyrite burial over the past million years could have caused the observed P_{O_2} decline. The ~2-million-year (+1.5/−0.5 million years) (*26*) geological residence time of O_2, combined with the decline in $\delta O_2/N_2$ of 8.4‰ per million years, indicates that O_2 sinks were 1.7% larger than sources over the past 800,000 years (*27*). We now explore possible causes for this drawdown, examining first the impact of changing erosion rates and second the impact of global cooling on P_{O_2}.

Global erosion rates influence the amount of rock weathered (consuming O_2) and sediment buried (releasing O_2). These rates have been suggested to have increased up to 100% in the Pleistocene relative to the Pliocene (*28*) [though this is debated (*29*)]. Thus, the possibility exists that increased Pleistocene sedimentary erosion and burial rates affected P_{O_2} levels. Indeed, Torres *et al.* (*30*) modeled that increasing erosion rates over the past 15 million years enhanced oxidation of sedimentary pyrite relative to burial so that P_{O_2} declined on average by 9 to 25‰ per million years. This is similar to the decline given by the ice core record (8.4‰ per million years). We note that whether increasing erosion rates cause P_{O_2} to decline (instead of increase) is unknown (*31*).

Large increases (e.g., 100%) in Pleistocene erosion rates, if they did occur, likely would have required processes that keep O_2 sources and sinks balanced within ~2% (the observed imbalance). Such processes could include the proposed P_{O_2}-dependent control of C_{org} burial fluxes on sedimentary phosphorus burial rates (*32*). Alternatively, sedimentary mineral surface area is known to positively correlate with total sedimentary C_{org} and pyrite content (*33*). Hedges and Kiel (*33*) proposed that the total eroded and total buried mineral surface areas today are about equal. If this was true in the past, the conservation of eroded versus newly generated mineral surface area may have acted to balance C_{org} and pyrite weathering and burial fluxes (and thus O_2 fluxes), regardless of global erosion rates (*33*).

Alternatively, on the basis of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ records from sedimentary carbonates, Shackleton (*2*) proposed that P_{O_2} declined over the Neogene as a result of oceanic cooling. He suggested the following feedback loop: Cooling increases O_2 solubility. This raises dissolved O_2 concentrations, which increases the volume of ocean sediment exposed to dissolved O_2 and thus also increases global aerobic C_{org} remineralization rates (*33*). On million-year time scales, C_{org} burial rates and, therefore, P_{O_2} and O_2 concentrations decline until seawater O_2 concentrations return to their initial (precooling) levels. At this new steady state, C_{org} burial rates have returned to their original values, but P_{O_2} is stabilized at a lower value.

Shackleton's hypothesis can be evaluated to first order in the context of the $\delta O_2/N_2$ data by using records of past ocean temperature. Specifically, temperatures in the deep (>1000 m depth) ocean were roughly constant from 24 to 14 million years ago (*34*, *35*). Assuming an O_2 residence time of ~2 million years and the hypothesis that changes in ocean temperature modulate P_{O_2}, then O_2 sources and sinks would have been in balance by 14 million years ago. The oceans have cooled on average by 0.3°C per million years over the past 14 million years and 0.5° to 1.1°C per million years over the past 5 million years (*34*, *35*). Cooling of 0.3° to 1.1°C per million years increases O_2 solubility by ~7 to 25‰ per million years (*36*). If dissolved O_2 concentrations remained constant (as this hypothesis requires), such changes in O_2 solubility necessitate a decline in P_{O_2} of ~7 to 25‰ per million years. These rates bracket the rate of decline given by the ice core record (8.4‰ per million years; Fig. 1A). We note that deep ocean cooling rates track average marine cooling rates, but not precisely, because modern deep waters form in and thus reflect the temperatures of high latitudes. Regardless, the critical point is that this simple calculation is consistent with the ice core–derived $\delta O_2/N_2$ record and supports the hypothesis that global temperature stabilizes P_{O_2} on geological time scales through feedbacks associated with C_{org} burial rates.

A drop in P_{O_2} over the past 800,000 years due solely to changes in C_{org} burial versus oxidation rates (regardless of the cause) requires positive CO_2 fluxes (~3 × 10^{11} moles C per year) into the ocean and atmosphere (*19*). However, ice core records of past carbon dioxide partial pressures (P_{CO_2}) show no obvious change in the mean over

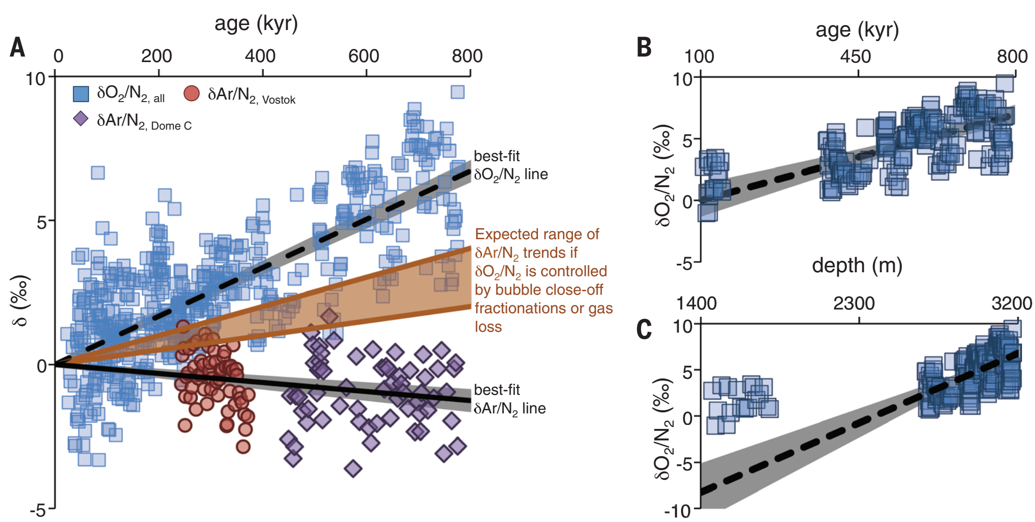

Fig. 2. Evidence that the observed decline in δO_2N_2 with time does not originate from either secular changes in bubble close-off fractionations or ice core storage. (**A**) $\delta Ar/N_2$ and $\delta O_2/N_2$ versus ice age. Bubble close-off processes and gas loss would cause $\delta Ar/N_2$ and $\delta O_2/N_2$ to covary with slopes of 0.3 to 0.6. The observed $\delta Ar/N_2$ trend does not overlap with these expected trends (orange wedge), indicating that such processes did not cause the decline in $\delta O_2/N_2$. (**B**) Dome C $\delta O_2/N_2$ versus ice age and (**C**) versus depth. Dotted lines were fit to ice >400,000 years old or >2600 m deep and extrapolated to younger ages or shallower depths. Extrapolations of the fits pass through the younger data (B) but miss the deeper data [beyond 4σ (C)], indicating depth-dependent glacial properties did not cause the decline in $\delta O_2/N_2$. Gray bands are 95% confidence intervals. Data are corrected for gravitational, interlaboratory, and bubble close-off fractionations (*19*).

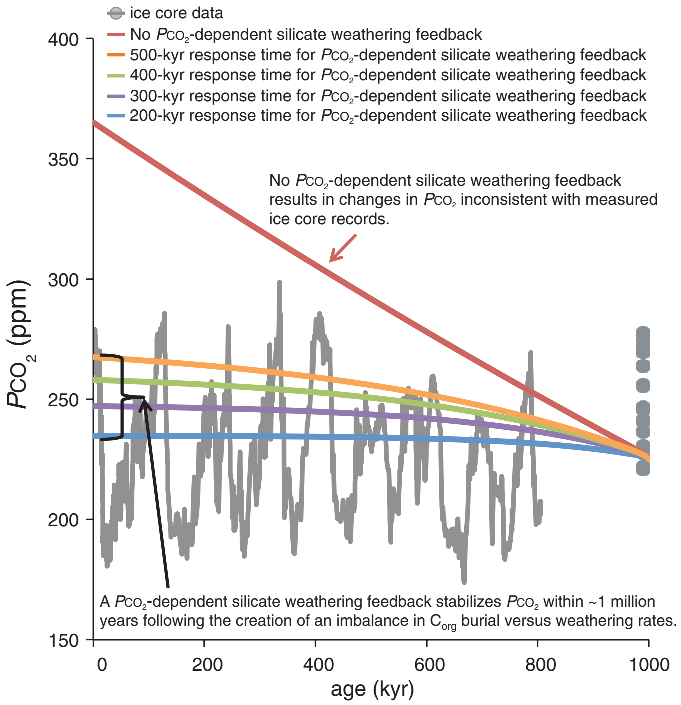

Fig. 3. Comparison of calculated and measured P_{CO_2} values due to declining P_{O_2} with and without a P_{CO_2}-dependent silicate weathering feedback. Inclusion of a silicate weathering feedback with geologically reasonable response times [200,000 to 500,000 years (*41*)] stabilizes P_{CO_2} within ~1 million years. Thus, increased silicate weathering rates could have compensated for enhanced CO_2 fluxes from increased net C_{org} oxidation more than 800,000 years ago. The P_{CO_2} records are continuous only from 800,000 years to the present. The model used to calculate P_{CO_2} values is described in (*19*); the measured P_{CO_2} values are from (*38*) and (*39*). ppm, parts per million.

the past 800,000 years (*37–39*) (Fig. 3). To understand how changes in P_{O_2} influence P_{CO_2}, we developed a simple model of the carbon cycle that allows for changes in weathering and burial rates of carbonates, C_{org}, and silicates (*19*). In the absence of any P_{CO_2}-dependent feedbacks, a constant decline in $\delta O_2/N_2$ of 8.4‰ over the past million years from a net imbalance in C_{org} fluxes causes P_{CO_2} to rise by ~140 parts per million over the same time frame. Such a rise is inconsistent with the P_{CO_2} record (Fig. 3). A P_{CO_2}-dependent silicate weathering feedback (*40*) can account for the higher CO_2 flux if silicate weathering is enhanced by ~6% relative to volcanic outgassing. For example, response times for silicate weathering of 200,000 to 500,000 years (*41*) stabilize P_{CO_2} levels within ~1 million years (Fig. 3).

Changes in Cenozoic climate began millions of years before the start of our ice core–based $\delta O_2/N_2$ record 800,000 years ago (e.g., *2, 30, 34, 35*). Thus, we suggest that modest enhancements in silicate weathering would already have stabilized the portion of the P_{CO_2} ice core record that is controlled by differences in C_{org} and pyrite burial and oxidation. Thus, the combination of changing P_{O_2} and constant average P_{CO_2} provides distinctive evidence for feedbacks that regulate P_{CO_2} on geologic time scales (*37*). Lastly, a 2% imbalance in O_2 fluxes results in only a ~0.1‰ shift in the $^{13}C/^{12}C$ ratio of buried carbon (*19*).

Our results provide a primary record of declining P_{O_2} over the past 800,000 years sustained by a ~2% imbalance between O_2 sources and sinks. Critically, this decline is consistent with previously proposed and relatively simple models that invoke either the effects of increased Pleistocene erosion rates or decreased ocean temperature to explain feedbacks in the global cycles of carbon, sulfur, and O_2—and the effects of both could have contributed to the observed decline in P_{O_2}. Regardless, creating primary records of past P_{O_2} is the necessary first step in identifying the fundamental processes that regulate P_{O_2} on geological time scales. Given evidence that both global erosion rates and temperature have changed markedly over the Cenozoic (*42*), the ideas presented here may have implications for the history of P_{O_2} beyond the Pleistocene.

REFERENCES AND NOTES

1. L. R. Kump, R. M. Garrels, *Am. J. Sci.* **286**, 337–360 (1986).
2. N. Shackleton, *Geol. Soc. Lond. Spec. Publ.* **26**, 423–434 (1987).
3. R. A. Berner, D. E. Canfield, *Am. J. Sci.* **289**, 333–361 (1989).
4. L. A. Derry, C. France-Lanord, *Paleoceanography* **11**, 267–275 (1996).
5. K. W. Hansen, K. Wallmann, *Am. J. Sci.* **303**, 94–148 (2003).
6. N. M. Bergman, T. M. Lenton, A. J. Watson, *Am. J. Sci.* **304**, 397–437 (2004).
7. P. G. Falkowski *et al.*, *Science* **309**, 2202–2204 (2005).
8. R. S. Arvidson, F. T. Mackenzie, M. Guidry, *Am. J. Sci.* **306**, 135–190 (2006).
9. R. A. Berner, *Geochim. Cosmochim. Acta* **70**, 5653–5664 (2006).
10. R. A. Berner, *Am. J. Sci.* **309**, 603–606 (2009).
11. I. J. Glasspool, A. C. Scott, *Nat. Geosci.* **3**, 627–630 (2010).
12. R. Tappert *et al.*, *Geochim. Cosmochim. Acta* **121**, 240–262 (2013).
13. M. L. Bender, *Earth Planet. Sci. Lett.* **204**, 275–289 (2002).
14. K. Kawamura *et al.*, *Nature* **448**, 912–916 (2007).
15. M Suwa, M. L. Bender, *Quat. Sci. Rev.* **27**, 1093–1106 (2008).
16. A. Landais *et al.*, *Clim. Past* **8**, 191–203 (2012).
17. L. Bazin *et al.*, *Clim. Past* **12**, 729–748 (2016).
18. M. E. Smith, thesis, Princeton University, Princeton, NJ (1998).
19. Materials and methods are available as supplementary materials on *Science* Online.
20. M. Battle *et al.*, *Nature* **383**, 231 (1996).
21. M. Bender, T. Sowers, V. Lipenkov, *J. Geophys. Res. Atmos.* **100**, 18651–18660 (1995).
22. T. Kobashi *et al.*, *Atmos. Chem. Phys.* **15**, 13895–13914 (2015).
23. J. P. Severinghaus, R. Beaudette, M. A. Headly, K. Taylor, E. J. Brook, *Science* **324**, 1431–1434 (2009).
24. H. Craig, Y. Horibe, T. Sowers, *Science* **242**, 1675–1678 (1988).
25. R. A. Berner, *Geology* **34**, 413–415 (2006).
26. H. D. Holland, *Geochim. Cosmochim. Acta* **66**, 3811–3826 (2002).
27. The imbalance is calculated as follows: The total imbalance (moles per million years) for O_2 is 0.0084 × n_{O_2}, where n_{O_2} is the total number of moles of O_2 in the atmosphere. The O_2 flux is n_{O_2} divided by its residence time. The residence time of O_2 is about 2 million years. The percent imbalance is the total imbalance divided by the total flux, or $0.0084n_{O_2}/(n_{O_2}/2)$ = 0.017 (1.7%).
28. F. Herman *et al.*, *Nature* **504**, 423–426 (2013).
29. J. K. Willenbring, F. von Blanckenburg, *Nature* **465**, 211–214 (2010).
30. M. A. Torres, A. J. West, G. Li, *Nature* **507**, 346–349 (2014).
31. A. S. Colman, F. T. Mackenzie, H. D. Holland, *Science* **275**, 406–407 (1997).
32. P. Van Cappellen, E. D. Ingall, *Science* **271**, 493–496 (1996).
33. J. I. Hedges, R. G. Keil, *Mar. Chem.* **49**, 81–115 (1995).
34. C. H. Lear, H. Elderfield, P. A. Wilson, *Science* **287**, 269–272 (2000).
35. B. Cramer, K. Miller, P. Barrett, J. Wright, *J. Geophys. Res. Oceans* **116**, C12023 (2011).
36. H. E. Garcia, L. I. Gordon, *Limnol. Oceanogr.* **37**, 1307–1312 (1992).
37. R. E. Zeebe, K. Caldeira, *Nat. Geosci.* **1**, 312–315 (2008).
38. B. Bereiter *et al.*, *Geophys. Res. Lett.* **42**, 542–549 (2015).
39. J. A. Higgins *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **112**, 6887–6891 (2015).
40. J. C. Walker, P. Hays, J. Kasting, *J. Geophys. Res.* **86**, 9776–9782 (1981).
41. D. Archer, *J. Geophys. Res. Oceans* **110**, C09S05 (2005).
42. M. Raymo, W. F. Ruddiman, *Nature* **359**, 117–122 (1992).

ACKNOWLEDGMENTS

D.A.S. acknowledges funding from a National Oceanic and Atmospheric Administration Climate & Global Change postdoctoral fellowship. J.A.H. and M.L.B. acknowledge support from National Science Foundation grant ANT-1443263. All data presented are available in the supplementary materials. We thank W. Fischer, I. Halevy, N. Planavsky, J. Severinghaus, and D. Sigman for helpful discussions and three anonymous reviewers for helpful comments on the manuscript. D.A.S., J.A.H., and M.L.B. conceived the study and wrote the manuscript. D.A.S., J.A.H., M.L.B., and Y.Y. analyzed the data. G.B.D. measured the Dome C $\delta Ar/N_2$ data. The views expressed in this article are those of the authors and do not necessarily represent the views of the Department of Energy or the U.S. Government.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/353/6306/1427/suppl/DC1
Materials and Methods
Figs. S1 to S6
Tables S1 to S3
References (*43–78*)

25 February 2016; accepted 2 August 2016
10.1126/science.aaf5445

Science

A Pleistocene ice core record of atmospheric O_2 concentrations

D. A. Stolper, M. L. Bender, G. B. Dreyfus, Y. Yan and J. A. Higgins

Science **353** (6306), 1427-1430.
DOI: 10.1126/science.aaf5445

Science (print ISSN 0036-8075; online ISSN 1095-9203) is published by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. The title *Science* is a registered trademark of AAAS.