Supplementary Materials for

Two Modes of Change in Southern Ocean Productivity
Over the Past Million Years

S. L. Jaccard,* C. T. Hayes, A. Martínez-García,

*Corresponding author. E-mail: samuel.jaccard@erdw.ethz.ch

Published 22 March 2013, Science 339, 1419 (2013)
DOI: 10.1126/science.1227545

This PDF file includes:

Materials and Methods
Figs. S1 to S3
References
Supporting Online Material for

“Two modes of change in Southern Ocean ocean productivity over the past million years”


1. Material and Methods

ODP Site 1094 is located in the Atlantic sector of the Southern Ocean (53.2°S, 05.1°E; water depth 2850 m), south of the present-day position of the Polar Frontal Zone and about 2° north of the average limit of winter sea-ice (Fig. 1). The core contains undisturbed diatomaceous ooze sequences with discontinuous carbonate-bearing intervals and occasional ice-rafted debris (IRD) layers. The stratigraphy is based on planktonic foraminifera δ¹⁸O (S1, S2) correlation to the EDC ice core age scale (S3) assuming an in-phase relationship (Fig. S1). Sedimentation rates are high, typically ranging between < 10 - 50 cm*kyr⁻¹, for glacial and peak interglacial intervals, respectively.

Relative sedimentary elemental concentrations (Ca, Fe, Ba) were measured with an Aavatech profiling X-ray Fluorescence (XRF) core scanner at Bremen University at a 1-2 cm (i.e. submillennial) resolution. Absolute elemental concentrations of major elements (Fe, Ca) were measured by ICP-OES (Varian Vista Pro) while minor elements (Ba) were measured by ICP-MS (Perkin-Elmer ELAN 9000) by ALS Chemex Ltd, North Vancouver, Canada. Accuracy was better than 5% and 2%, respectively, for replicate measurements. The biogenic fraction of Ba (bioBa) was determined by normalization by Fe; bioBa = Baᵣₑ₋(Fe * (Ba/Fe)ᵢₙ₉ₒᵣᵦ), with (Ba/Fe)ᵢₙ₉ₒᵦ = 0.0157 (S4). Comparison between discrete ICP-MS and relative Ba/Fe and Ca/Fe measurements shows a significant statistical correlation (Fig. S2A & B). Similarly, discrete coulometric CaCO₃ quantifications show a high degree of fidelity when compared to core-scanning XRF Ca/Fe determinations (Fig. S2C). For the analysis of phytoplankton pigment transformation products (chlorins) sediment samples were freeze-dried and solvent extracted using an Accelerated Solvent Extractor (ASE). The absorbance of the organic extracts at the
characteristic wavelength of the chlorins was measured with a Photodiode Array Detector (PDA) coupled to an HPLC system following the methods described in detail by (S5). $^{230}$Th-normalized fluxes (S6) were evaluated as described in Chase et al. (2003). Concentrations of U and Th isotopes were determined by isotope dilution ICP mass spectrometry (S7). The authigenic U content of each sample was evaluated using the measured $^{232}$Th and $^{238}$U concentrations. Measured $^{230}$Th concentrations were corrected for the detrital contribution using $^{232}$Th and for ingrowth produced by authigenic U, and then decay corrected to the time of deposition to derive $^{230}$Th-normalized fluxes. Concentrations of biogenic opal were measured by alkaline extraction and molybdate-blue spectrophotometry (S8). All variables were determined on aliquots of the same homogenized sample.

2. Figures

![Graph](image)

**Fig. S1** Final solution of the age model reappraisal resulting from fine-tuning the ODP 1094 planktonic $\delta^{18}$O composite record (purple) (S1, S2) to EDC $\delta^{D}$ (grey) (S3). The correlation factor exceeds 0.90. The fine bars represent the tie-points defined to tune both records.
Fig. S2 Comparison between XRF-scanning elemental- and log ratios (S9) and discrete ICP-MS and CaCO₃ measurements.
Fig. S3 Compilation of available bioBa flux and MAR record from the Atlantic sector of the Southern Ocean. Core locations are shown on sea-surface temperature field, dissolved nitrate and silic acid climatologies, respectively. Each record is on its own, independent age model. (A) ODP 1094/TN57-13PC (53.2°S, 05.1°E; water depth 2850 m; this study); (B) PS1768 (53°36.4’S, 4°28’E, 3270m) (S10); (C) PS1772 (55°27.5’S, 1°09.8’E, 4135m) (S10); (D) PS1575 (62°50.97’S, 43°20.013’W, 3461m) (S11); (E) PS1821 (67°03.092’S, 37°28083’E, 4027m) (S11); (F) PS1648 (69°44.040’S, 06°31.048’W, 2529m) (S11). All records show consistently high export during early interglacials and low values during ice ages.
3. References


S3. J. Jouzel et al., Orbital and Millenial Antarctic Climate Variability over the Past 800,000 Years. Science 317, 793 (2007).


