

# Organic carbon paleo-pCO<sub>2</sub> and marine-ice core correlations and chronology

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**Abstract.** Here we present evidence that marine organic matter  $\delta^{13}\text{C}$  measurements can closely reproduce the Vostok ice core CO<sub>2</sub> record and, in addition, can be used to evaluate the absolute Vostok chronology and the transfer of that chronology between the marine and terrestrial realm. Our data supports recent speculations that the base of the Vostok ice core (2755 m) is still within oxygen isotope stage 7, in agreement with recent orbitally-tuned ice core chronologies.

## Introduction

To examine phase relationships between atmospheric climate proxies from ice cores (CO<sub>2</sub>, CH<sub>4</sub>, air temperature, etc.) and ocean climate proxies from marine sediments (ice volume, ocean circulation, sea surface temperature, etc.), one needs a common temporal framework. Obviously, a time scale based on a rheological ice flow model has no inherent relevance to a deep sea core. *Petit et al.* [1990] developed the first "common" chronology by correlating the Vostok dust record with a magnetic susceptibility record from a Southern Ocean piston core. Similar chronologies [*Pichon et al.*, 1992; *Shackleton et al.*, 1992] were based on correlation of the Vostok air temperature record with Southern Ocean sea surface temperature records. More recently *Sowers et al.* [1993] correlated the  $\delta^{18}\text{O}$  of atmospheric O<sub>2</sub> ( $\delta^{18}\text{O}_{\text{atm}}$ ) trapped in the Vostok ice core to the seawater  $\delta^{18}\text{O}$  ( $\delta^{18}\text{O}_{\text{sw}}$ ) record preserved in calcitic deep sea sediment. The  $\delta^{18}\text{O}_{\text{atm}}$  primarily reflects variations in  $\delta^{18}\text{O}_{\text{sw}}$  although variations in terrestrial productivity can result in significant differences between the two records [*Sowers et al.*, 1993]. Here we present a common chronology for marine and ice core records based on a correlation of the atmospheric pCO<sub>2</sub> record trapped by ice to the surface ocean pCO<sub>2</sub> record inferred from marine organic matter  $\delta^{13}\text{C}$ . While this method also has its uncertainties, it provides one more technique for evaluation of ocean-ice correlations.

## Ice Core Chronologies

In *Jouzel et al.* [1993], Vostok CO<sub>2</sub>, CH<sub>4</sub>,  $\delta\text{D}$ , dust, and  $\delta^{18}\text{O}_{\text{atm}}$  data extending to 2544 meters depth were presented along with an updated glaciological chronology referred to as the EGT (extended glaciological timescale). The  $\delta^{18}\text{O}_{\text{atm}}$  record is here plotted to the EGT timescale in Figure 1a (along with the SPECMAP  $\delta^{18}\text{O}_{\text{sw}}$  stack) and the Vostok pCO<sub>2</sub> record is plotted versus the EGT timescale in Figure 2a. In their 1993 study, *Jouzel* and colleagues also suggest a possible correlation between marine and ice core records (Figure 3 of that paper) based on

correlation of  $\delta^{18}\text{O}_{\text{sw}}$  and  $\delta^{18}\text{O}_{\text{atm}}$  (Figure 1b). This correlation, referred to in Figures 1b and 2b as the TIELINE timescale, implies that the deepest  $\delta^{18}\text{O}_{\text{atm}}$  samples (at 2544 m) fall near the top of oxygen isotopic stage 7.4. In Figure 2b, the Vostok CO<sub>2</sub> record is plotted to the TIELINE chronology.

Recently published  $\delta\text{D}$  data from deeper sections of the ice core [*Vostok Project Members*, 1995] suggests that the TIELINE correlation to the marine record is problematic; the interval inferred to be stage 8 (about 2600 m) appears much too short in the ice core record. *Jouzel* and colleagues speculate that the deepest ice yet recovered (2755m) may still be in stage 7 (specifically stage 7.5) rather than in stage 9 as implied by the *Jouzel et al.* [1993] TIELINE timescale. We made this assumption and correlated the  $\delta^{18}\text{O}_{\text{atm}}$  and  $\delta^{18}\text{O}_{\text{sw}}$  records accordingly in Figure 1c. We refer to this time scale as the EOS chronology and show the Vostok pCO<sub>2</sub> record to this timescale in Figure 2c. Note that recent orbitally tuned timescales for Vostok [*Bender et al.*, 1995; *Waelbroeck et al.*, in press; *Jouzel et al.*, submitted] are most consistent with our EOS timescale.

## Surface Ocean pCO<sub>2</sub>

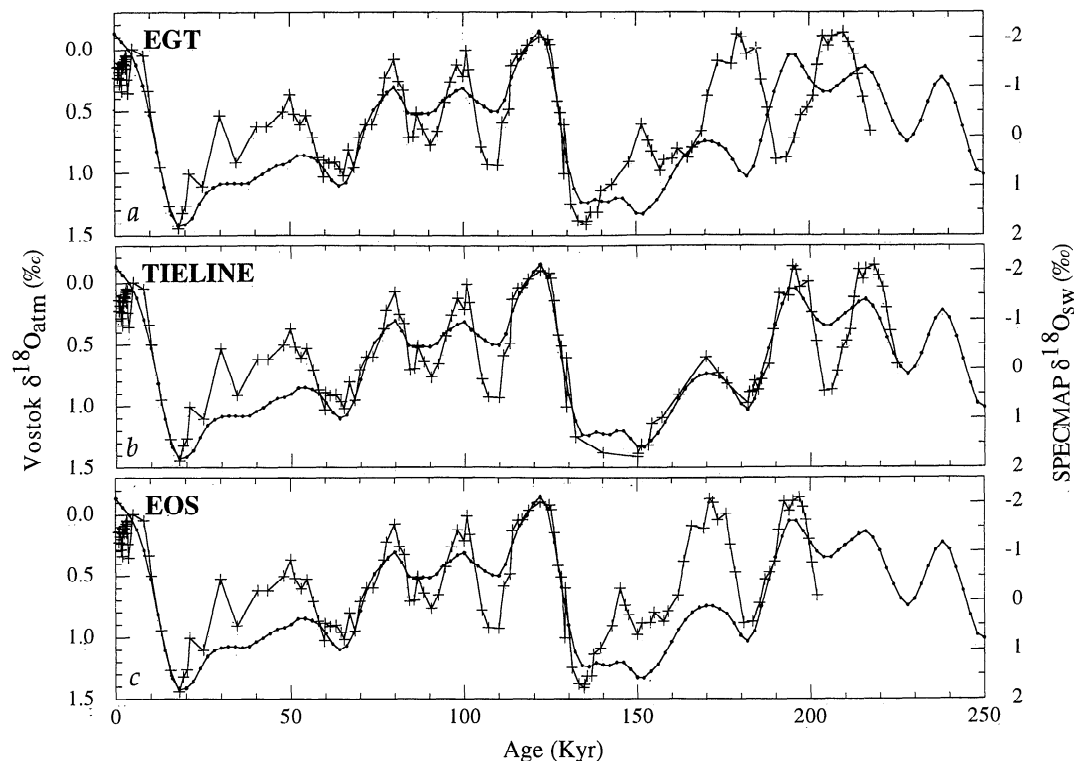
The record of surface ocean pCO<sub>2</sub> variation (Figure 2) can be used to evaluate the published and proposed marine-ice core stratigraphic correlations (e.g. Figure 1). On average, surface ocean pCO<sub>2</sub> is in thermodynamic equilibrium with the atmosphere, with most areas of the ocean within 35 ppm of atmospheric levels [*Keeling*, 1968; *Tans et al.*, 1990; *Inoue and Sugimura*, 1992; *Takahashi et al.*, 1993]. Areas of pronounced air/sea disequilibrium are found where seasonal upwelling results in CO<sub>2</sub> supersaturation (as typically observed in equatorial regions) or where productivity results in undersaturation (typically observed at high latitudes). A number of studies have now demonstrated that  $\delta^{13}\text{C}$  in marine plankton, including suspended and sedimentary particulate organic matter (POM), varies inversely as a function of ambient CO<sub>2(aq)</sub> concentration in the surface water, [CO<sub>2(aq)</sub>] [*Mizutani and Wada*, 1982; *Arthur et al.*, 1985; *McCabe*, 1985; *Popp et al.*, 1989; *Jasper and Hayes*, 1990; *Rau et al.*, 1991, 1992; *Francois et al.*, 1993; *Rau*, 1994]. Surface ocean [CO<sub>2(aq)</sub>] and pCO<sub>2</sub> are interrelated via a temperature and salinity dependent solubility factor,  $\alpha$ , such that ocean pCO<sub>2</sub> = [CO<sub>2(aq)</sub>]/ $\alpha$ . By measuring the  $\delta^{13}\text{C}$  of marine organic matter preserved in deep sea sediments and using the above relationships, a number of studies have reconstructed ocean pCO<sub>2</sub> levels in the past [*Freeman and Hayes*, 1992; *Stott*, 1992; *Jasper et al.*, 1994]. In particular, many sediment core  $\delta^{13}\text{C}_{\text{POM}}$  records show an ~1.5‰ decrease across the last glacial-interglacial (G-I) transition corresponding to a mean surface ocean pCO<sub>2</sub> increase of about 80  $\mu\text{atms}$ , as confirmed from ice cores [e.g. *Rau et al.*, 1991; *Rau*, 1994; *Muller et al.*, 1994; *Raymo et al.*, 1996].

In all three panels of Figure 2, estimated surface water pCO<sub>2</sub> levels from western equatorial Pacific ODP Site 806 (0°N,

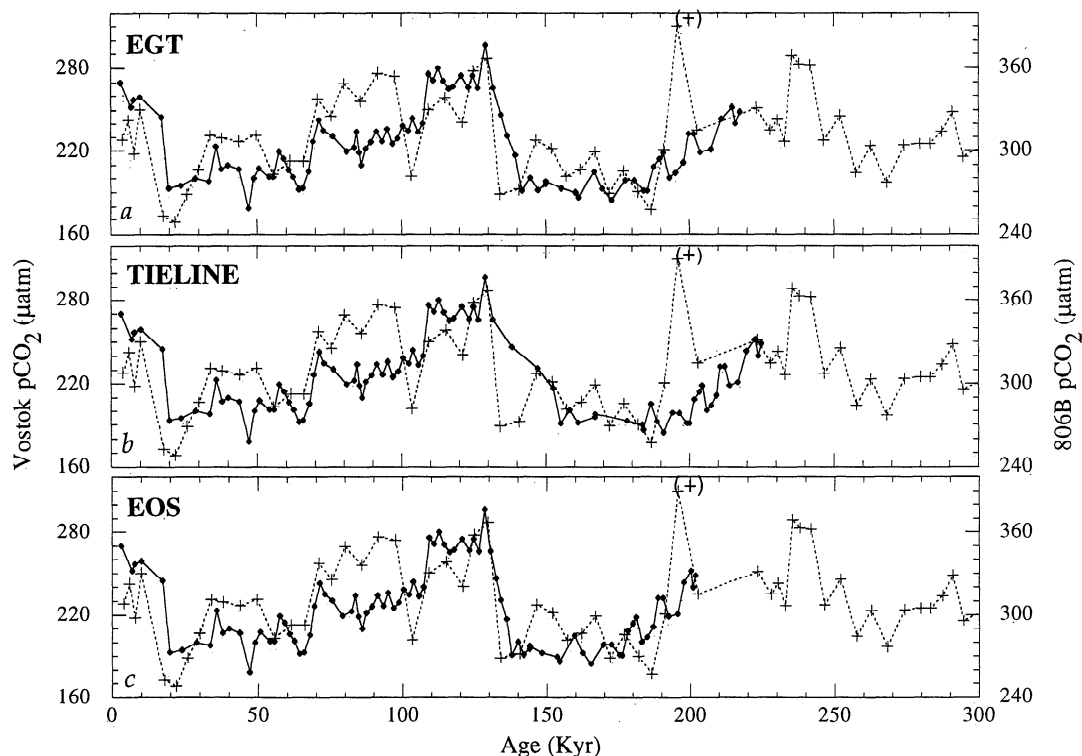
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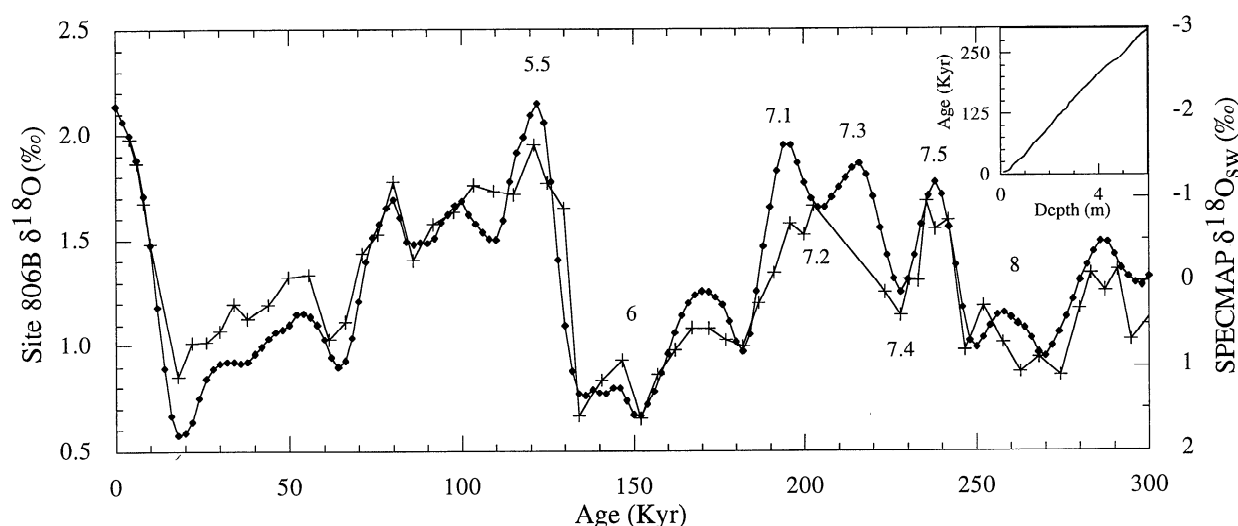
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**Figure 1.** a)  $\delta^{18}\text{O}_{\text{atm}}$  from Vostok (+) plotted to the EGT timescale of *Jouzel et al.* [1993] versus SPECMAP  $\delta^{18}\text{O}_{\text{sw}}$  stack (•) of *Imbrie et al.* [1984]; b) same as Figure 1a only time scale for  $\delta^{18}\text{O}_{\text{atm}}$  below stage 5e is based on inferred correlation of marine-ice records shown in Figure 3 of *Jouzel et al.* [1993]. The time scale for  $\delta^{18}\text{O}_{\text{atm}}$  above stage 5e is from *Sowers et al.* [1993]; c) same as Figure 1a only  $\delta^{18}\text{O}_{\text{atm}}$  timescale derived from an alternate marine-ice core correlation suggested by *Vostok Project Members* [1995].



**Figure 2.** Time scales for the ice core pCO<sub>2</sub> record (•) are the same as in Figure 1. In each panel we have also plotted (to the SPECMAP time scale, Figure 3) the Site 806 surface ocean pCO<sub>2</sub> record (+) from *Raymo et al.* [1996] (note offset of vertical axes). Sedimentation rates at Site 806 are about 1.9 cm/Kyr and the average sampling interval is ~5 Kyr. Note that all marine pCO<sub>2</sub> estimates are based on triplicate determinations of  $\delta^{13}\text{C}_{\text{POM}}$  ( $1\sigma = 0.18\text{‰}$ ). The flier in parentheses falls well above the top of the graph (529  $\mu\text{atm}$ ). The estimation of pCO<sub>2</sub> includes a number of potential errors including analytical (above), SST for solubility, and regression of modern  $\delta^{13}\text{C}_{\text{POM}}$  against  $[\text{CO}_{2(\text{aq})}]$ . The overall error, dominated by the regression error, is about  $\pm 65$  ppm ([*Raymo et al.*, 1996], error varies slightly with temperature). This error is artificially large due to the use of indirect and/or non-contemporaneous estimates of  $[\text{CO}_{2(\text{aq})}]$  in the modern oceanographic data set upon which the  $\delta^{13}\text{C}_{\text{POM}}$  regression is based [*Rau*, 1994].



**Figure 3.** Correlation of planktonic  $\delta^{18}\text{O}_{\text{sw}}$  record from Site 806 (‰ relative to PDB [•]) to the SPECMAP stack (in normalized ‰ units [•]). This correlation is the basis of the time scale used for the Site 806  $\text{pCO}_2$  record shown in Figure 2. The gap in the Site 806 record between about 200 and 230 Kyr is where a whole round section of core was removed for pore fluid studies. Inset shows mapping function of correlation and selected isotopic stages are labeled.

159°E, 2520 meters depth) are plotted to the SPECMAP  $\delta^{18}\text{O}$  chronology [Imbrie *et al.*, 1984]. The time scale was generated by correlation of the planktonic  $\delta^{18}\text{O}$  data [Berger *et al.*, 1993] to the SPECMAP stack (Figure 3). The mapping function for this correlation is shown as an inset in Figure 3. In Figure 2, the Vostok  $\text{pCO}_2$  record is plotted to three different time scales; the EGT chronology (Figure 2a), the TIELINE chronology (Figure 2b), and the EOS chronology (Figure 2c). The ice core accumulation rates for each of these three chronologies are shown in Figure 4. Before evaluating the marine-ice core correlations it is important to note two things about the ocean  $\text{pCO}_2$  record. First, the region of Site 806 is generally supersaturated by about 20–60 ppm, on average, with respect to atmospheric  $\text{pCO}_2$  due to weak equatorial upwelling [Keeling, 1968; Inoue and Sugimura, 1992] and the estimated Holocene

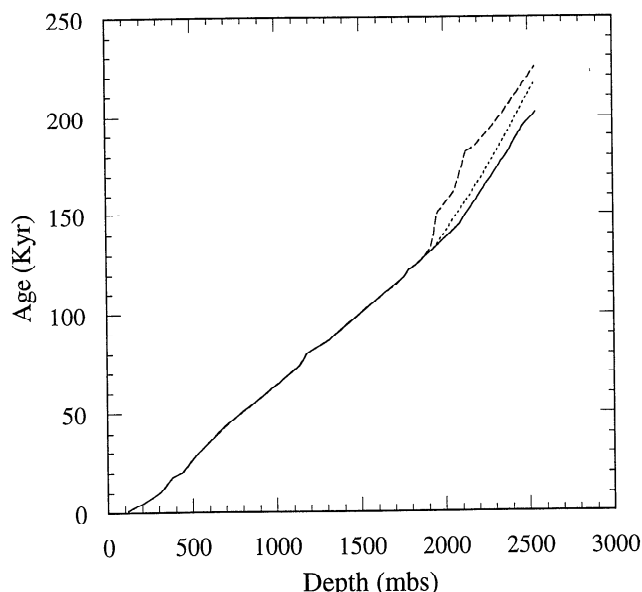
ocean  $\text{pCO}_2$  values (between 300–340 ppm) fall within this range. Second, we have linearly detrended the last 400 Kyr of the 806  $\text{pCO}_2$  record (by 84 ppm; higher estimated  $\text{pCO}_2$  values in the middle Pleistocene which may be due to long term changes in upwelling, productivity, or diagenesis at this site [Raymo *et al.*, 1996]).

### Marine-Ice Core Correlations

The ocean and atmosphere  $\text{pCO}_2$  records shown in Figure 2 share many similarities including G-I terminations which are of approximately the same magnitude, about 80–100 ppm. As with the  $\delta^{18}\text{O}_{\text{atm}}$  and  $\delta^{18}\text{O}_{\text{sw}}$  records, however, the correlation is not perfect (e.g. parts of stage 5) since factors other than gas exchange with the atmosphere influence surface water  $\text{pCO}_2$  (for instance, changes in productivity and upwelling strength; [Raymo *et al.*, 1996] and references therein). Nevertheless, of the three proposed Vostok chronologies, the EOS and EGT timescales clearly present the least conflict with the 806  $\text{pCO}_2$  record. The TIELINES timescale shows significant mismatches on the stage 7/6 and 6/5 boundaries.

Comparing the EOS and EGT timescales, EOS appears to exhibit a slightly better fit on Termination II, the stage 6/5 transition. However, more convincing support for this timescale is that the EGT timescale clearly gives an unlikely correlation between  $\delta^{18}\text{O}_{\text{atm}}$  and  $\delta^{18}\text{O}_{\text{sw}}$  within stage 7 (Figure 1a). Thus, the  $\text{pCO}_2$  data from Site 806 argues against the  $\delta^{18}\text{O}_{\text{atm}}$ -based TIELINES timescale, while the  $\delta^{18}\text{O}_{\text{atm}}$  data would appear to rule out the EGT timescale. Based on these comparisons, we predict that new ice core  $\text{CO}_2$  data, from below 2544 m, will support the EOS chronology; published  $\text{pCO}_2$  data from Vostok has just reached stage 7.1 and the deeper isotopic temperature maximum at 2755 m depth corresponds to stage 7.5. Further, this chronology implies a significant biological overprint of the  $\delta^{18}\text{O}_{\text{atm}}$  record within stage 6 (Figure 1c). The EOS chronology, supported by correlation of marine and ice core  $\text{CO}_2$  and  $\delta^{18}\text{O}$  data, is also consistent with recently derived chronologies based on orbital tuning of the ice core climate records [Bender *et al.*, 1995; Waelbroeck *et al.*, in press; Jouzel *et al.*, submitted].

With respect to the *relative* correlation of marine and ice core climate records, we believe the EOS correlation of Figures 1c and



**Figure 4.** Ice accumulation rates at Vostok for three ice core chronologies used in Figures 1 and 2. Solid line = EOS, dotted line = EGT, dashed line = TIELINE.

2c to be the most likely and present the ice core and marine records to the SPECMAP timescale using this correlation. On the other hand, the *absolute* chronology may be closer to the glaciological EGT time scale, however, we doubt this since such a time scale would imply greater accumulation rate perturbations in Vostok (Figure 4) and in almost any oceanographic record correlated to the EGT time scale, including Site 806. In closing, comparison of ocean and atmospheric pCO<sub>2</sub> records provides an additional means of evaluating correlations between marine and ice core climate records, a task that will undoubtedly increase in difficulty as deeper, more compacted ice is retrieved from Vostok. In addition, while all the pCO<sub>2</sub> proxy techniques have uncertainties, we hope the data presented here will convince a skeptical reader that organic carbon based paleo-pCO<sub>2</sub> proxies hold promise for the investigation of pre-Quaternary ocean and atmosphere pCO<sub>2</sub> changes.

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