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A methane-based time scale for Vostok ice

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Abstract

Tuning the Vostok methane signal to mid-July 30°N insolation yields a new ice-core gas time scale. This exercise has two rationales: (1) evidence supporting Kutzbach's theory that low-latitude summer insolation in the northern hemisphere controls the strength of tropical monsoons, and (2) interhemispheric CH_4 gradients showing that the main control of orbital-scale CH_4 variations is tropical (monsoonal) sources. The immediate basis for tuning CH_4 to mid-July insolation is the coincident timing of the most recent (pre-anthropogenic) CH_4 maximum at 11,000–10,500 calendar years ago and the most recent July 30°N insolation maximum (all ages in this paper are in calendar years unless specified as ^{14}C years).

The resulting CH_4 gas time scale diverges by as much as 15,000 years from the GT4 gas time scale (Petit et al., Nature 399 (1999) 429) prior to 250,000 years ago, but it matches fairly closely a time scale derived by tuning ice-core $\delta^{18}O_{atm}$ to a lagged insolation signal (Shackleton, Science 289 (2000) 1897). Most offsets between the CH_4 and $\delta^{18}O_{atm}$ time scales can be explained by assuming that tropical monsoons and ice sheets alternate in controlling the phase of the $\delta^{18}O_{atm}$ signal.

The CH_4 time scale provides an estimate of the timing of the Vostok CO_2 signal against SPECMAP marine $\delta^{18}O$, often used as an index of global ice volume. On the CH_4 time scale, all CO_2 responses are highly coherent with SPECMAP $\delta^{18}O$ at the orbital periods. CO_2 leads $\delta^{18}O$ by 5000 years at 100,000 years (eccentricity), but the two signals are nearly in-phase at 41,000 years (obliquity) and 23,000 years (precession). The actual phasing between CO_2 and ice volume is difficult to infer because of likely SST overprints on the SPECMAP $\delta^{18}O$ signal. CO_2 could lead, or be in phase with, ice volume, but is unlikely to lag behind the ice response.

0. Introduction

Ice cores contain an incredible variety of climatic signals that have had a major impact on climate research. Over time spans of 400,000 years or more, ice-core signals show obvious cyclic behavior concentrated within the range of astronomically calculated changes in Earth's orbit, from 20,000 to 100,000 years. To date, however, it has proven difficult to realize the full promise of these ice-core signals because the time scale has not been sufficiently accurate. Without a consistently high level of accuracy (to within a few thousand years), it is difficult to assess how each ice-core signal is partitioned among the orbital periods. More critically, it is impossible to fix the orbital-scale phasing between ice-core signals and insolation forcing, as well as other climatic responses such as ice volume. Accurate phasing (lead/lag) information is vital to efforts to establish cause-and-effect (forcing-and-response) climatic relationships.

Section 1 of this paper reviews the history of development of time scales for Vostok ice record, including estimates of the uncertainties associated with each method. Section 2 sets out the rationale for creating a new Vostok gas time scale based on monsoon forcing of atmospheric methane (CH_4) concentrations. Section 3 makes an initial assessment of this new CH_4 time scale and concludes that it is preferable to the GT4 (gas) time scale of Petit et al. (1999). Section 4 focuses on differences between the CH_4 time scale and the generally similar $\delta^{18}O_{atm}$ time scale of Shackleton (2000) and concludes that the CH_4 time scale provides a more plausible explanation for the small offsets. Section 5 uses the CH_4 time scale as a basis to define the orbital-scale

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phasing of CO_2 relative to SPECMAP $\delta^{18}O$. Finally, Section 6 summarizes factors that make it difficult to infer the phasing of CO_2 against ice volume.

1. History of time scales for Vostok ice

Early time scales for the Vostok ice record across the last full interglacial–glacial cycle were derived from ice-flow/ice-accumulation models; these are based on the initial rate of accumulation of snow in the area feeding ice to the Vostok core site, and on subsequent ice thinning determined from an ice-flow model (Lorius et al., 1985). The initial rate of accumulation is estimated from $\delta^{18}O$ values in the ice using modern spatial relationships. The flow model also requires assumptions about the form of the surface and bedrock topography upstream from the ice-core site.

This initial time scale for Vostok ice raised concerns because the next-to-last deglaciation occurred more than 10,000 years before the seemingly equivalent feature in the marine $\delta^{18}O$ signal and was thus out of phase with respect to the presumed insolation forcing. This mismatch was lessened when Jouzel et al. (1993) altered the time scale of Lorius et al. (1985) by incorporating considerably higher accumulation rates in features considered equivalent to marine isotopic stages 6 and 5.

Petit et al. (1999) published signals from the full length of the Vostok ice core. For the upper 110,000 years of the record, they used a slightly adjusted version of the ice-flow/ice-accumulation time scale from Jouzel et al. (1993). They pinned the rest of the ice time scale (termed "GT4") to levels assumed to represent 110,000 and 423,000 years ago, based on inferred correlations to the marine $\delta^{18}O$ record. Between these points, they estimated ages by calculating ice thinning based on a flow model, with adjustments for basal melting and sliding. A second method for dating ice cores is by counting annual layers preserved in rapidly deposited ice. This method cannot be used in the slowly deposited Vostok ice, but time scales developed in the last 15,000 years from Greenland ice can be transferred to Vostok using globally correlative climate signals such as methane.

A third approach is to correlate ("tune") climate-sensitive proxies within Vostok ice to climatic signals in marine sediments. In effect, this method transfers the orbitally tuned time scale of the marine record to the ice core. Marine records are tuned by matching the filtered 41,000-year and 23,000-year components of marine $\delta^{18}O$ signals to assumed forcing at the corresponding orbital periods, with lags appropriate to the long time constants of ice sheets.

Several such correlations to the marine record have been attempted. Petit et al. (1999) correlated the dust concentration in Vostok ice with a magnetic susceptibility record in Southern Ocean core RC11-120, based on the assumption that the marine magnetic susceptibility signal at 41°S is a proxy for dust deposition. Pichon et al. (1992) and Waelbroeck et al. (1995) correlated deuterium (δD) in Vostok ice with diatom-based estimates of sea surface temperature in marine cores from middle latitudes of the Southern Ocean based on the assumption that mid-latitude changes in sea-surface temperature correlate with air-temperature changes at 80°S.

Sowers et al. (1993) tuned the $\delta^{18}O$ of atmospheric O_2 in Vostok ice to a marine $\delta^{18}O$ target signal in Pacific core V19–30. First, they tried to remove the imprint of bottom-water temperature changes from the benthic foraminiferal $\delta^{18}O$ signal to isolate $\delta^{18}O_{sw}$ (the mean $\delta^{18}O$ value of seawater) as an ice-volume tuning target. Raymo and Horowitz (1996) used an inferred marine $\delta^{13}C$ proxy for past CO_2 values to correlate with the Vostok CO_2 record, but also checked matches of Vostok $\delta^{18}O_{atm}$ against marine $\delta^{18}O$ values. Shackleton (2000) tuned Vostok $\delta^{18}O_{atm}$ to a synthetic orbital insolation signal used as a target. He relied on the age of the major $\delta^{18}O_{atm}$ change at the last deglaciation in annually layered GISP ice to set the phase of the precession and obliquity components of the $\delta^{18}O_{atm}$ signal relative to insolation.

Each technique for estimating ages carries inherent uncertainties. These errors are difficult to establish for ice-flow/ice-accumulation models, but were estimated by Petit et al. (1999) as ranging from ± 5000 to 15,000 years in different parts of the Vostok record. Uncertainties in counting annual layers can be estimated by comparing different signals in the same core or the same signal in nearby cores (Meese et al., 1997). These range from 100 to 200 years back to 12,000 years ago to about 5% of the absolute age down to 55,000 years ago (the level by which annual layering cannot be reliably detected). Techniques that link ice-core signals to marine records produce errors in the correlation process, with progressively larger errors for successively more dissimilar signals. These techniques also implicitly incorporate the 3000-year to 5000-year uncertainty in orbital tuning of the marine record (Imbrie et al., 1984). Correlations of $\delta^{18}O_{atm}$ to marine $\delta^{18}O_{sw}$ also introduce an uncertainty of ± 500 years in the turnover time of O_2 in the atmosphere (Sowers et al., 1993). In addition, correlations between ice and gas phases within Vostok ice may be in error by ± 2000 years (Sowers et al., 1993).

2. Rationale for tuning ice-core methane (CH_4) to orbital insolation

We present here a new gas time scale for Vostok based on a simple and well-justified approach: tuning the methane (CH_4) gas signal in Vostok ice to mid-July insolation at 30°N. This method is based on two assumptions. The first assumption is that the CH_4 signal is mainly a response to the strength of low-latitude monsoons, with secondary input from boreal sources (Raynaud et al., 1988; Chappellaz et al., 1990; Blunier et al., 1995; Brook et al., 1996). Strong summer monsoons deliver moisture to southeast Asia, India, and northern Africa, and the monsoonal rains fill lakes and wetlands that become sources of methane as vegetation decays in reducing conditions. Modeling of CH_4 gradients between Greenland and Antarctic ice over the last 40,000 years indicates that the tropics have been the dominant source of methane over orbital time scales (Chappellaz et al., 1997; Brook et al., 2000).

The second assumption is that tropical monsoons are driven by low-latitude summer insolation with a dominant orbital precession signal. This assumption builds on the orbital monsoon hypothesis first proposed by Kutzbach (1981). This hypothesis has since been supported by a wide array of evidence, including tropical lake levels (Street-Perrott and Harrison, 1984; Kutzbach and Street-Perrott, 1985), Nile-induced stratification of the Mediterranean Sea (Rossignol-Strick et al., 1982), and influxes of freshwater diatoms blown from African lakes into Atlantic sediments (Pokras and Mix, 1987).

This tuning exercise requires two key choices of an insolation "tuning target": (1) a critical latitude, and (2) a critical season or month. To guide this choice, we compare the timing of insolation signals calculated in calendric years against the calendric age of the most recent CH_4 maximum in the GRIP ice core from Greenland as determined from counting annual layers.

The most recent CH_4 maximum in the GRIP ice core prior to the anthropogenic era is a broad maximum from 14,500 to 8500 years ago (Fig. 1). This peak is interrupted by an abrupt CH_4 minimum during the Younger Dryas event near 12,000 years ago, and is followed by a smaller minimum just before 8000 years ago. Despite these interruptions, the wave-like form of the orbital-scale peak remains evident. Peak CH_4 values are centered near 11,000 to 10,500 years ago. Attempts to refine this estimate of the age of the CH_4 maximum using a spline fit would be hampered by the presence of the abrupt Younger Dryas event and the rapid deglacial CH_4 increase near 14,500 years ago. At this level in the ice, the age offset between the CH_4 gas and the ice in which it is trapped is about 50 years (Blunier et al., 1995).

This age for the CH_4 maximum matches the timing of the most recent mid-July insolation maximum at low and middle latitudes (Berger and Loutre, 1992). Because a family of precession curves exists for each season and month due to the slow progression of the solstices and equinoxes around the elliptical orbit, it is necessary to select one of these monthly signals as critical. The June

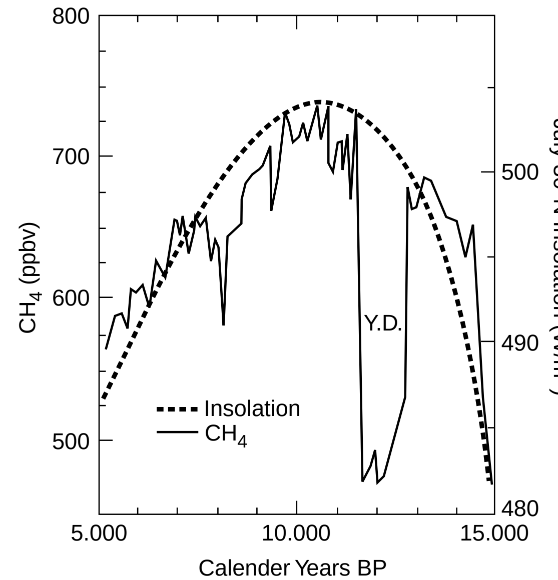

Fig. 1. Comparison of CH_4 trends between 15,000 and 5000 years ago (based on a composite trend from the GRIP ice core assembled by Chappellaz et al., 1997) and July insolation at 30°N (from Berger and Loutre, 1992). YD marks the Younger Dryas event.

21 summer solstice is often used as a reference for analyzing insolation changes, but mid-July insolation appears to provide the optimal match to the GRIP CH_4 peak (Fig. 1). GCM analyses of summer monsoon forcing often choose the June/July/August season, centered on mid-July, as the critical season (Prell and Kutzbach, 1987).

We chose 30°N as the critical insolation latitude to balance the combined effect of several land masses heated by low-latitude insolation. North Africa lies almost entirely in the tropics (<23°N), but Asia extends through the subtropics and far into higher latitudes. Across much of the north tropics and subtropics, a different choice of latitude would not significantly alter the shape (or timing) of the tuning target. But at latitudes above 50°N, insolation signals begin to take on more of the signature of the 41,000-year obliquity signal, and this can nudge specific precessional maxima and minima toward slightly younger or older ages.

This rationale for tuning methane to July 30°N insolation might be challenged in several ways. One basis for challenge is that some climatic proxies linked to tropical monsoons reach maximum responses later than the ice-core CH_4 maximum. Radiocarbon dating shows that closed-basin lakes in North Africa reached their highest levels between 9000 and 6000 ^{14}C years ago (Street-Perrott and Harrison, 1984) and that Nile River runoff from monsoonal regions of northeast Africa created organic-rich sapropel muds in the Mediterranean Sea from 9000 to 7000 ^{14}C years ago (Thunell and Williams, 1989). Even when converted to calendar years, these responses occurred 10,000 to 7500 years ago, well after the July insolation maximum from 11,000 to 10,500 years ago. Similar lags occur in upwelling proxies and pollen influxes off the Somali coast of eastern Africa (Prell, 1984; Prell and van Campo, 1986). These lags, which occur in and around Africa, may reflect external climatic influences on the African monsoon such as the lingering effects of northern ice sheets or North Atlantic SST (deMenocal and Rind, 1996), or the delayed timing of the 23,000-year SST maximum in the eastern tropical Atlantic from which the monsoon draws latent heat (McIntyre et al., 1989).

On close inspection, however, many of the best-dated African lake records resemble the methane trends plotted in Fig. 1, showing major increases in monsoonal moisture 14,500 years ago, maximum lake levels by 11,000 years ago, and high lake levels until 5000 to 4000 years ago (Gasse, 2000). In contrast, the Mediterranean sapropels occur well toward the end of this moist interval, suggesting that they are a lagging indicator of monsoon conditions.

In any case, the recent CH_4 maximum in the GRIP ice core used to set the timing of our tuning exercise is well dated, and other evidence from Asia supports this timing. Planktonic foraminiferal $\delta^{18}O$ signals in South China Sea cores show negative departures from typical $\delta^{18}O$ values during the last deglaciation (Wang et al., 1999). These deviations are interpreted as salinity decreases caused by excess river inflow caused by south Asian monsoons. This inferred monsoon signal first appeared 15,000 years ago, markedly increased in strength just before 13,000 years BP, and gradually ended after 9000 years ago. Given the large wetland expanse in southern Asia, Asian CH_4 sources probably dominated the ice-core CH_4 signal.

A second possible challenge to our rationale is that part of the CH_4 signal comes from boreal wetland sources far from regions controlled by tropical monsoons. But CH_4 gradients between Greenland and Antarctic ice suggest that tropical methane sources were twice as large as those north of 30°N during both the last-glacial CH_4 minimum and the late-deglacial CH_4 maximum (Chappellaz et al., 1997; Brook et al., 2000). This indicates that tropical monsoons dominated the CH_4 signal through a range of climatic changes.

In addition, the mid-July insolation peak that produces maximum amounts of CH_4 from tropical monsoons at the 23,000-year cycle should also drive a coincident CH_4 influx from boreal regions. Mid-summer heating of the Asian continent should warm the chilly northern wetlands, stimulate a brief mid-summer pulse of microbial activity, and liberate maximum amounts of boreal CH_4. The mid-July phasing of the CH_4 maximum in Fig. 1 is consistent with the idea of coincident mid-summer CH_4 influxes from tropical and boreal sources.

A third potential criticism is that melting of CH_4-bearing clathrates, either those frozen in terrestrial sediments at high latitudes or in shallow marine sediments at any latitude, could be another possible source of atmospheric CH_4. The rapid changes in CH_4 during the last 15,000 years shown in Fig. 1 could be interpreted as lending credibility to this idea. To date, however, ice-core studies have not favored this possibility. The character of the record in Fig. 1 is more easily interpreted as one in which cold-climate CH_4 minima interrupt longer-term orbital-scale CH_4 maxima, rather than as warm-climate pulses of excess CH_4 expelled from clathrates. In addition, Brook et al. (2000) noted that even the most rapid CH_4 declines were spread over 200 to 300 years, an interval significantly longer than the abrupt shifts of other ice-core signals towards colder conditions, and consistent with the time scale for ecosystem adjustments to suddenly imposed reductions in tropical moisture.

In any case, the slowly deposited ice at Vostok acts as a low-pass filter and smoothes most millennial-scale CH_4 fluctuations, leaving behind a record mainly of orbital-scale changes. Over this time scale, Chappellaz et al. (1997) inferred that any clathrate contribution to ice-core CH_4 must have arrived as a relatively steady input over orbital-scale intervals. As such, this input would be indistinguishable from monsoonal inputs.

Our method carries less uncertainty than any other ice-dating technique. The CH_4 signal plotted in Fig. 1 is in error by at most 150 ± 50 years (Meese et al., 1997). Visual inspection shows that it would be difficult to shift our choice of July as the critical insolation month by more than ± 300 to 400 years without harming the match shown in Fig. 1. (Such a shift equates to less than a week if converted to equivalent time in the precessional cycle.) In addition, monthly (and seasonal) insolation signals have no significant dating error across the time range examined here (Berger and Loutre, 1992). As a result, errors in our choice of tuning target are unlikely to exceed ± 500 years.

The largest potential source of error in our procedure (assuming the validity of our basic rationale) arises from the process of linking maxima and minima in the CH_4 signal with the precisely dated insolation signal (Table 1). The Vostok CH_4 signal is sampled at an average interval of <1500 years over the last 350,000 years, with the spacing ranging from <1000 years in the upper part of the record to about 2000 years in the older portion. This sample spacing introduces an average uncertainty of ± 750 years across the record, with a range from ± 500 years in the upper part to ± 1000 years in the older part. Combined with the ± 500-year error in our initial choice of the tuning target, we estimate that the errors associated with our method could optimally be as small as ± 1000–2000 years.

Across some intervals, however, our method could have larger errors. Precession-driven CH_4 maxima and minima are not well developed during the glacial parts

Table 1
CH_4 time scale for Vostok ice

Depth in ice (m)	Age (10^3 yr)	Feature correlated
149.2	0	—
321.2	11	Max
506.4	22	Min
664.1	32	Max
748.3	45	Min
860.6	58	Max
1087.2	70	Min
1237.2	82	Max
1338.2	93	Min
1526.2	104	Max
1557.4	115	Min
1893.4	131	Max
2030.9	137	Midpoint
2137.1	149	Max
2177.3	161	Min
2363.0	174	Max
2437.0	185	Min
2525.0	196	Max
2557.7	208	Min
2621.7	219	Max
2698.0	230	Min
2771.2	240	Max
2830.4	251	Min
2857.5	265	Max
2911.4	278	Min
2944.5	290	Max
2994.5	301	Min
3051.5	312	Max
3054.5	320	Min
3078.5	328	Midpoint
3109.5	334	Max
3138.5	338	Midpoint
3165.5	344	Min

Feature correlated specifies maxima, minima or transition midpoints in both the 30°N insolation curve and the Vostok CH_4 record used as control points for correlation, with linear interpolation of intervening levels.

of the Vostok record, such as the intervals around 40,000, 150,000, and 260,000 years ago. During these intervals, it is difficult to link the CH_4 record to precessional insolation. As a result, errors larger than 5000 years (1/4 of a precessional cycle) are not impossible. For the rest of the record, errors greater than 2000 years are unlikely. Finally, as is the case for all tuning techniques, our method is vulnerable to the assumption that the phase of the monsoon may have varied through time because of variable influences of other parts of the climate system (ice sheets, SST, etc).

3. Initial assessment of the CH_4 time scale

A time-series comparison shows the tuned correlation between Vostok CH_4 and 30°N July insolation (Fig. 2a). Both signals show distinct amplitude modulation at the precessional cycle. As noted above, the major correlation uncertainties occur within low-amplitude CH_4 oscillations during full-glacial conditions. In addition, some CH_4 peaks are interrupted by brief minima, but the basic precessional wave pattern remains apparent through most of the record. We call this time scale the "CH_4 time scale" (Table 1).

The Vostok record below 3180 m ice depth (350,000 years age) is omitted because neither the CH_4 signal nor the 30°N insolation tuning target has sufficiently distinctive amplitude variations within this age range to permit credible tuning. It is also unclear whether the Vostok record reaches the bottom of marine isotopic stage 11 (Petit et al., 1999).

Cross-spectral analysis confirms that the strong 23,000-year power in the tuned CH_4 signal is in phase, and highly coherent, with precessional insolation (Fig. 2b–d). The largest mismatches in amplitude occur on CH_4 minima, most of which are rectified at minimum values of 400–420 ppb, even when insolation falls to very low values. Amplitude mismatches between insolation and CH_4 also occur near terminations, with somewhat deeper minima just prior to deglaciations and disproportionately strong CH_4 maxima early in the following interglaciations. These mismatches suggest that factors other than insolation also effect the amplitude of early interglacial CH_4 maxima.

The main difference between the two signals is the concentration of CH_4 power at 100,000 and 41,000 years, periods that are not prominent in the July 30°N insolation tuning signal (Fig. 2b). The 100,000-year signal is in phase with eccentricity, largely as a result of the common eccentricity modulation of both CH_4 and of the precessional insolation signal used as the tuning target. The 41,000-year CH_4 signal lags well behind insolation at the obliquity period (Fig. 2c) and is nearly in phase with the 41,000-year component of SPECMAP $\delta^{18}O$. This phasing suggests that the 41,000-year CH_4 signal largely reflects an overprint of ice volume (or some other glacial boundary condition) on methane emissions from tropical and/or boreal wetlands (Prell and Kutzbach, 1987).

The methane record plotted at the CH_4 time scale is compared with that of the GT4 time scale of Petit et al. (1999) in Fig. 3. Because the CH_4 time scale used CH_4 gas for tuning, we use the GT4 gas time scale for this comparison, rather than the GT4 time scale for ice. The GT4 gas time scale was derived by subtracting 2000 to 6000 years from the time scale for ice, with larger differences during glacial intervals of slow ice accumulation (Petit et al. 1999).

For most of the record back to 250,000 years ago, the CH_4 and GT4 time scales are similar, with age departures of no more than 5000 to 10,000 years, and generally only a few thousand years (Fig. 3a). The ages of many CH_4 maxima and minima in the GT4 time scale only needed to be shifted by 1000 to 3000 years to create

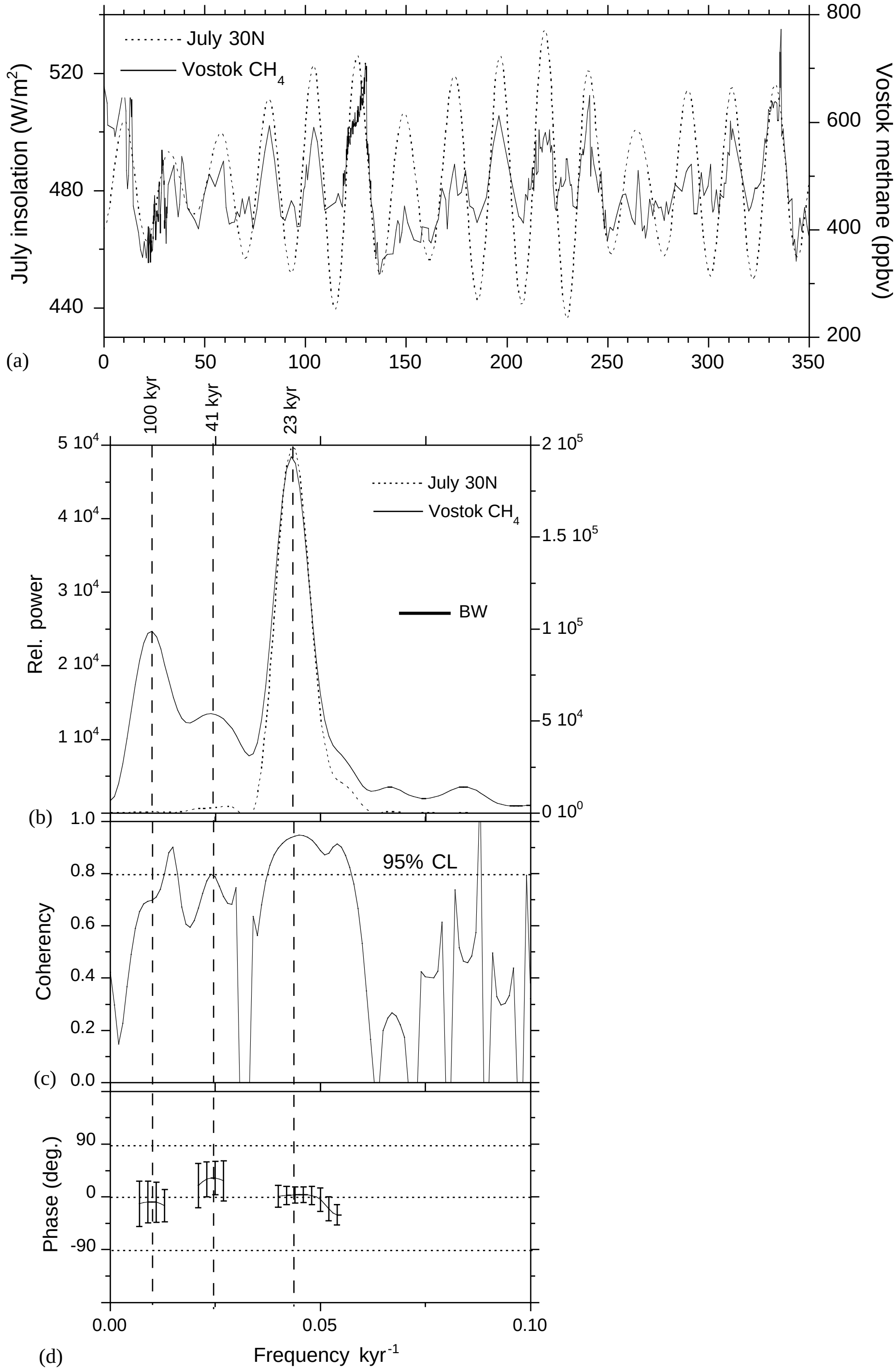

Fig. 2. Comparison of Vostok CH_4 (plotted on the CH_4 time scale) and July 30°N insolation for the last 350,000 years: (a) Time series; (b–d) Cross-spectral analysis; (b) power spectra; (c) coherence between CH_4 and insolation; and (d) relative phasing at orbital periods. Spectral analysis followed Blackman–Tukey method, with 1/3 lags. Phases at the major orbital periods shown with 95% confidence intervals.

the CH_4 time scale. These age offsets lie well within the uncertainties estimated by Petit et al. (1999).

The CH_4 time scale produces several relatively abrupt changes in ice accumulation rate compared to the GT4 time scale. Although these might result from "over-tuning" the Vostok methane record to the July 30°N insolation target, none of these changes produces suspicious-looking distortions of other (untuned) gas signals from Vostok ice (Sections 4 and 5).

Prior to 250,000 years ago, the ages derived from the CH_4 time scale diverge from those of the GT4 time scale by much larger amounts averaging near 15,000 years (Fig. 3a). Over much of this interval, the GT4 time scale yields a climatically implausible phasing between

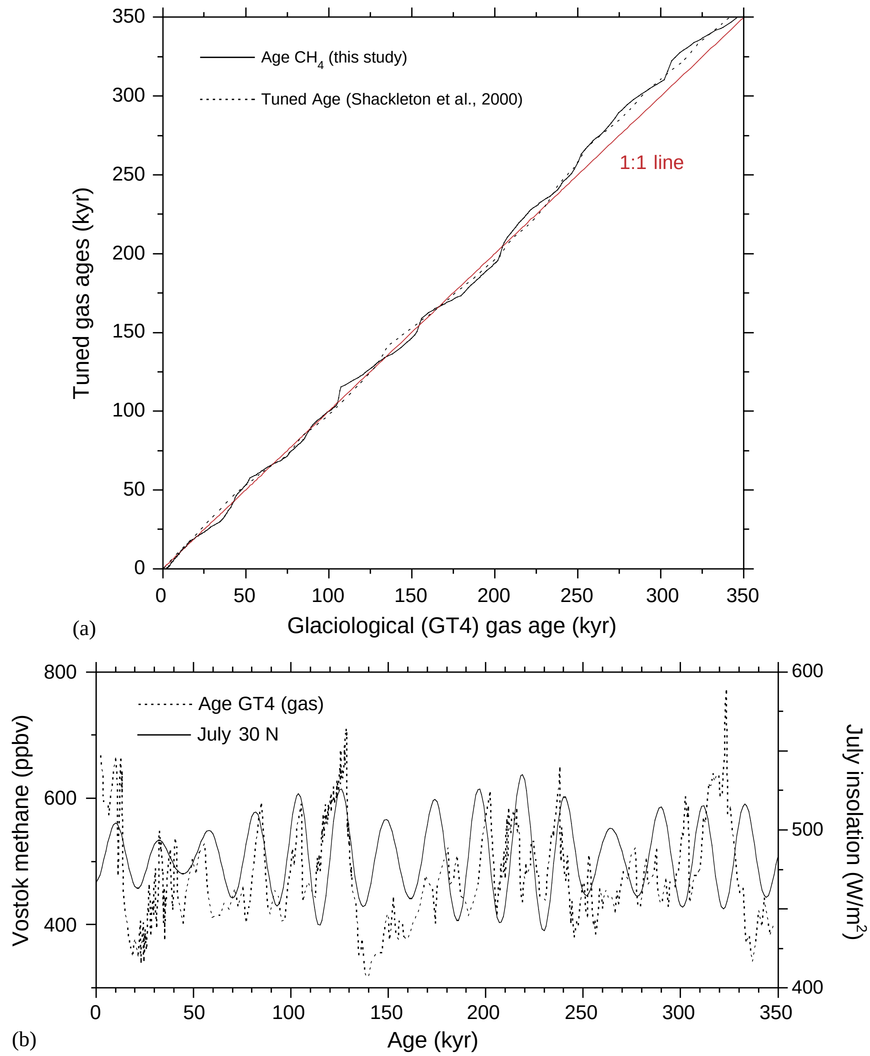

Fig. 3. Comparison of GT4, CH_4 and $\delta^{18}O_{atm}$ time scales: (a) Diagonal (1:1) line based on Vostok GT4 gas time scale (Petit et al., 1999) is used as a reference for departures of ages in other time scales. Solid line: CH_4 time scale from this paper; dotted line: $\delta^{18}O_{atm}$ time scale of Shackleton (2000); (b) Time series of Vostok CH_4 on the GT4 time scale against July insolation.

Vostok CH_4 values and summer (July 30°N) insolation (Fig. 3b): maxima in CH_4 are often aligned with minima in July insolation, a phasing opposite what would be expected for northern hemisphere insolation control of monsoonal and boreal CH_4 input.

Also plotted in Fig. 3a are age-depth offsets between the $\delta^{18}O_{atm}$ time scale of Shackleton (2000) and the GT4 time scale. For levels prior to 250,000 years ago, the $\delta^{18}O_{atm}$ and CH_4 time scales agree in showing ages considerably older than those from GT4. This convergence supports the conclusion that the GT4 age estimates for this older part of the Vostok record are substantially in error.

The fact that the CH_4 and $\delta^{18}O_{atm}$ time scales generally differ from each other by only a few thousand years points to major progress toward the goal of obtaining a Vostok time scale sufficient to analyze the phasing of orbital-scale ice-core signals. It also suggests that it would be worthwhile to take a closer look at the differences between these two time scales.

4. Assessment of the $\delta^{18}O_{atm}$ Signal

The $\delta^{18}O_{atm}$ time scale is based on tuning ice-core $\delta^{18}O_{atm}$ to a synthetic insolation signal containing both precession and obliquity, and incorporating phase lags appropriate to the slow responses of ice sheets to orbital forcing at these periods. In contrast, as summarized in Section 2, the CH_4 time scale is based on tuning CH_4 to a precession-dominated 30°N July insolation with no lags. Although the $\delta^{18}O_{atm}$ and CH_4 time scales are based on different tuning rationales, they differ in age by less than 5000 years through most of the last 350,000 years, and by an average of less than 500 years.

Despite this overall agreement, larger offsets between the two time scales do occur in some intervals (Fig. 3a). One clue to the origin of these offsets is that the relative phasing of the CH_4 and $\delta^{18}O_{atm}$ signals varies through time, with the two signals sometimes closely in phase, and sometimes well out of phase (Fig. 4a). These shifting offsets cannot be an artifact of the time scale used: both CH_4 and $\delta^{18}O_{atm}$ are recorded in the same gas phase of the same ice core, and so similar offsets must exist for any time scale chosen.

An initial way to explore the cause of these offsets is to assume that the CH_4 time scale correctly fixes the age of Vostok ice, and then examine resulting changes in the phase of the $\delta^{18}O_{atm}$ signal through time. We compare the $\delta^{18}O_{atm}$ signal (plotted on the CH_4 time scale) to mid-July insolation at 30°N (Fig. 4b) and to the SPECMAP $\delta^{18}O$ curve (Fig. 4c).

The $\delta^{18}O_{atm}$ trend shows fairly systematic phase offsets with respect to both insolation and SPECMAP $\delta^{18}O$ (as also noted by Jouzel et al., 2002). During peak interglacial substages (marine isotopic stages 5.5, 9.3, and, to some extent, 7.3), the $\delta^{18}O_{atm}$ signal is approximately in phase with July insolation (Fig. 4b), but it generally lags behind insolation during late-interglacial substages (5.1, 5.3, 7.1, and 9.1) and glacial isotopic stages (4–2, 6 and 8). Conversely, $\delta^{18}O_{atm}$ leads SPECMAP $\delta^{18}O$ during and just after peak-interglacial substages (Fig. 4c), but is roughly in phase during most

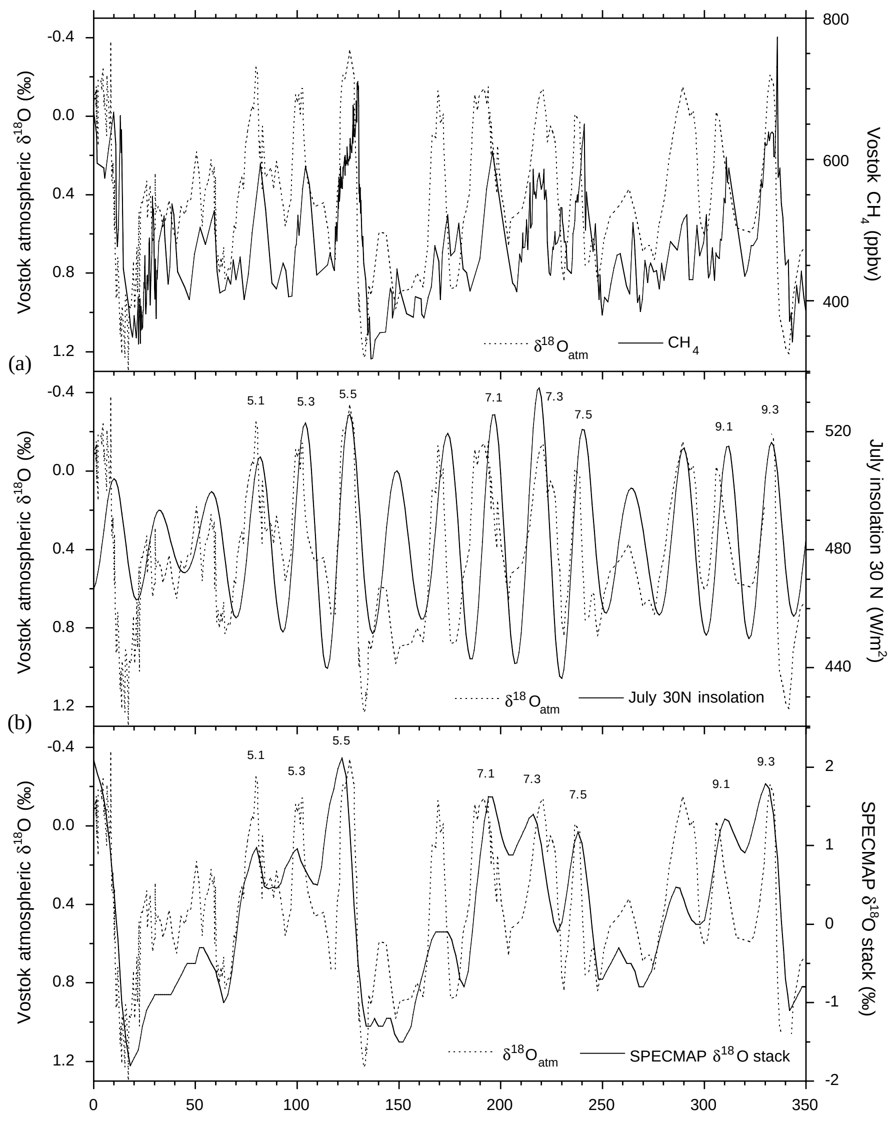

Fig. 4. Evaluation of the Vostok $\delta^{18}O_{atm}$ signal by time-series comparison with: (a) Vostok CH_4 (both records plotted on the CH_4 time scale); (b) July 30°N insolation ($\delta^{18}O_{atm}$ plotted on the CH_4 time scale and July 30°N insolation from Berger and Loutre (1992); (c) $\delta^{18}O_{atm}$ plotted on the CH_4 time scale and SPECMAP $\delta^{18}O$ plotted on the time scale of Imbrie et al. (1984).

late-interglacial and glacial isotopic stages. These shifts in $\delta^{18}O_{atm}$ phasing appear to be linked to climate in a systematic way, but why?

Two climatic factors control $\delta^{18}O_{atm}$ variations over orbital time scales. The $\delta^{18}O$ value of oxygen in the atmosphere ($\delta^{18}O_{atm}$) responds to the globally averaged $\delta^{18}O$ value of marine sea water ($\delta^{18}O_{sw}$), with an estimated lag today of about 1200 years caused by the turnover time of O_2 in the atmosphere (Bender et al., 1994). Because $\delta^{18}O_{sw}$ is a measure of the size of global ice sheets (and excludes the effect of ocean temperature on regional marine $\delta^{18}O$ measurements), one of the two major climatic controls on $\delta^{18}O_{atm}$ is thus global ice volume.

The second control operates through the "Dole effect" (Dole et al., 1954). Fractionation during marine and terrestrial photosynthesis and respiration causes modern $\delta^{18}O_{atm}$ to be offset by +23.5‰ compared to $\delta^{18}O_{sw}$. Sowers et al. (1993) found that the estimated size of this effect varied over orbital time scales by about 1‰, roughly the same magnitude as changes in $\delta^{18}O_{sw}$ caused by ice sheets. Bender et al. (1994) argued that these changes in the Dole effect probably resulted from varying photosynthesis and respiration in the tropical monsoon system. Thus, changes in tropical monsoons are the second likely climatic control on $\delta^{18}O_{atm}$.

We propose that the variable timing of the $\delta^{18}O_{atm}$ signal relative to insolation and SPECMAP $\delta^{18}O$ (Fig. 4) is caused primarily by changes in the relative influence of these two controls on $\delta^{18}O_{atm}$ through time. During and just after peak-interglacial stages, the $\delta^{18}O_{atm}$ signal responds in phase with July insolation and CH_4 because the monsoon system controls $\delta^{18}O_{atm}$ in the absence of large ice sheets. At these times, the $\delta^{18}O_{atm}$ signal joins CH_4 in following the fast response to insolation forcing and minimal lag typical of monsoons. In addition, the rapid and early ice melting typical of terminations brings the $\delta^{18}O_{sw}$ component of the $\delta^{18}O_{atm}$ signal into close alignment with the monsoonal Dole component.

At other times, including the later parts of interglacial stages and the glacial stages, the $\delta^{18}O_{atm}$ signal responds with a phase closer to that of marine $\delta^{18}O_{sw}$ (ice volume), because the monsoon weakens from its peak-interglacial strength and because ice-sheet variations grow large enough to become the major control of the $\delta^{18}O_{atm}$ signal. At these times, the $\delta^{18}O_{atm}$ signal takes on the slow response to insolation changes typical of ice sheets, and it lags behind the monsoon-controlled CH_4 signal. In summary, the phasing of the $\delta^{18}O_{atm}$ signal is monsoon-dominated when ice sheets are small, and ice-dominated when ice sheets are larger.

Other evidence supports this interpretation. The size of the monsoonal Dole effect can be monitored by variations in amplitude of the $\delta^{18}O_{atm}$ signal in excess of those in the marine $\delta^{18}O_{sw}$ signal. Sowers et al. (1993) inferred that the largest (estimated) Dole effect occurred between peak-interglacial substages 5.5 and 5.4, accounting for 50% or more of the $\delta^{18}O_{atm}$ change (monsoon control). The smallest Dole effect occurs in late-interglacial substages and glacial stages, where it accounts for as little as 20 to 30% of the total (ice-sheet control).

We began this section by making the assumption that the ice-core methane signal has the constant phasing with July insolation forcing used in creating the CH_4 time scale. Now we test the opposite assumption: could the phasing of $\delta^{18}O_{atm}$ be constant and that of CH_4 variable?

The tuning strategy used by Shackleton (2000) gave the $\delta^{18}O_{atm}$ signal the same phasing as SPECMAP used for the marine $\delta^{18}O$ signal: a 5000-year lag of $\delta^{18}O$ behind June 21 precessional insolation and an 8000-year lag behind obliquity. He chose smaller marine $\delta^{18}O$ lags behind insolation than those in SPECMAP, but also incorporated the additional lag of $\delta^{18}O_{atm}$ behind marine $\delta^{18}O$. Because Shackleton tuned the $\delta^{18}O_{atm}$ signal primarily to orbital precession, the average lag of the $\delta^{18}O_{atm}$ signal behind insolation was about 5000 years.

If we accept Shackleton's choice of $\delta^{18}O_{atm}$ phasing as correct, how would it affect the timing of the CH_4 signal? During and just after peak interglaciations, when $\delta^{18}O_{atm}$ and CH_4 are in phase, CH_4 should share the same 5000-year lag behind June 21 insolation as the $\delta^{18}O_{atm}$ signal. For the remainder of each interglacial-glacial cycle, when CH_4 leads $\delta^{18}O_{atm}$ by about 5000 years, CH_4 should be approximately in phase with June 21 insolation.

But this pattern of variable CH_4 phasing makes little physical sense in climatic terms. Why would a monsoon-dominated CH_4 signal respond earlier when ice sheets are large, but later when ice sheets are small? If ice sheets have any effect on monsoon timing, it should be to retard them. We conclude that the differences between the CH_4 and $\delta^{18}O_{atm}$ time scales are more plausibly explained by variable controls on the phasing of the $\delta^{18}O_{atm}$ signal than by variable timing of the CH_4 signal.

What about the possibility that ice sheets can indeed cause delays in monsoon timing? If growing ice sheets do retard monsoons, then the phase of the CH_4 signal should shift to younger ages during glacial isotopic stages because of the larger lags behind insolation forcing. And if the gas-phase CH_4 signal has been shifted in this way, the $\delta^{18}O_{atm}$ signal must also shift to younger ages because it is recorded in the same bubbles. But such a shift in ice-core $\delta^{18}O_{atm}$ creates a major problem for its phase relationship with marine $\delta^{18}O$ (Fig. 4c). Any major shift of the ice-core $\delta^{18}O_{atm}$ signal to younger ages will make it lag marine $\delta^{18}O$ at most isotopic transitions. If this occurs, an implausible scenario is created: the ice-core $\delta^{18}O_{atm}$ signal now lags well behind its only known controlling processes: the monsoon signal (through the Dole effect), and the marine $\delta^{18}O$ signal. Because this scenario makes no sense, it seems unlikely that ice sheets can cause major lags in the monsoon-generated CH_4 signal.

Although it is difficult (impossible?) to show conclusively that the monsoon-dominated CH_4 signal retains the same phasing through all the complex changes occurring during glacial–interglacial climate cycles, the evidence reviewed above suggests that it is likely that the CH_4 signal retains a stable (or very nearly stable) phase through time. In summary, the time scales derived by tuning ice-core $\delta^{18}O_{atm}$ and CH_4 to insolation diverge from the time scale of Petit et al. (1999) prior to 250,000 years ago, but generally match each other to within a few thousand years back to 350,000 years ago. On average, the CH_4 time scale is just 450 years younger than the $\delta^{18}O_{atm}$ time scale of Shackleton (2000). If the smaller differences between the two tuned time scales are indeed caused mainly by variable climatic controls on $\delta^{18}O_{atm}$ phasing, the CH_4 time scale is the more accurate of the two. This level of accuracy (to within a few thousand years) allows a close examination of the phasing of other gases in Vostok ice.

5. Comparison of Vostok CO_2 Versus SPECMAP $\delta^{18}O$

Of all the signals recorded in Vostok ice, the concentration of carbon dioxide is the most important to global climate. Because the CO_2 signal was not used in the tuning process, it provides an independent way to evaluate the CH_4 time scale, in this case by comparison to the GT4 time scale of Petit et al. (1999). For cross-spectral comparisons, we omit levels above 5000 years because of likely human influences on CH_4 (Ruddiman and Thomson, 2001).

The concentration of spectral power for CO_2 at orbital periods is not much different for the CH_4 and GT4 time scales (Figs. 5 and 6). In the CH_4 time scale, the peaks at 100,000 and 41,000 years lose power compared to GT4, but a new peak emerges near 23,000 years. Also, compared to the $\delta^{18}O_{atm}$ time scale of Shackleton (2000), the CH_4 time scale has almost identical amounts of power at 100,000 and 41,000 years, but a substantially larger peak at 23,000 years. Because no a priori expectation exists about the "true" shape of the CO_2 signal, and the distribution of its power among the orbital periods, however, these comparisons of CO_2 spectra alone are not a revealing test of the CH_4 time scale.

A more diagnostic evaluation comes from comparing the relative timing of Vostok CO_2 and the SPECMAP marine $\delta^{18}O$ signal (Imbrie et al., 1984). Plotted on the CH_4 time scale (Fig. 5a), the CO_2 signal is visually similar to SPECMAP $\delta^{18}O$, with many of the most prominent isotopic transitions occurring nearly in phase. The largest exception is a CO_2 lead of 4000 to 5000 years at the isotope stage 6/5 deglaciation (termination II). In contrast, the CO_2 signal plotted on the GT4 time scale shows a more erratic pattern of leads and lags compared to SPECMAP $\delta^{18}O$ (Fig. 6a).

This improved correlation is confirmed in a quantitative way by cross-spectral analysis (Figs. 5b–d and 6b-d). The 23,000-year orbital period has a greatly improved coherency in the CH_4 time scale, and the already strong coherence of the 41,000-year and 100,000-year cycles in the GT4 time scale both increase in the CH_4 time scale. Because CO_2 was not used to tune the CH_4 time scale, the improved coherences at all three orbital periods are independent confirmation of the validity of the CH4 time scale. In comparison, the $\delta^{18}O_{atm}$ time scale from Shackleton (2000) has power at 23,000 years, but no distinct peak at that period.

The more similar phasing of the CO_2 and $\delta^{18}O$ signals resulting from the CH_4 (and $\delta^{18}O_{atm}$) time scale fits into a long trend in the history of Vostok time-scale development. Earlier time scales based on models of ice flow and accumulation (Lorius et al., 1985), and adjusted from ice age to gas age (Barnola et al., 1987), produced an irregular phasing between CO_2 and marine $\delta^{18}O$: large CO_2 leads occurred on terminations, but sizeable lags occurred at the marine isotopic stages 5/4 and 5e/5d transitions (times of inferred major ice-sheet growth). Later time scales (summarized in Section 2) generally tended to reduce this variability in phasing, and the CH_4 time scale devised here points to a still more consistent (in-phase) timing.

As noted earlier, no a priori basis exists for predicting the form of the CO_2 signal. Still, it makes good sense from a climate-theory viewpoint that the phasing between CO_2 and ice volume should be consistent rather than irregular. The relatively stable (and nearly in-phase) relationship across major $\delta^{18}O$ transitions in the CH_4 time scale is suggestive of a consistent physical relationship between CO_2, a major greenhouse gas, and $\delta^{18}O$, a primary indicator of climate. The increases in coherency at all three orbital periods provide further evidence of a more consistent physical link between CO_2 and SPECMAP $\delta^{18}O$ over the last 350,000 years.

For the CH_4 time scale, maximum coherencies occur at a CO_2 lead of 12° (1400 ± 1400 years) relative to SPECMAP $\delta^{18}O$ for the 41,000-year period and 31° (2000 ± 900 years) for the 23,000-year period. These phases for the $\delta^{18}O_{atm}$ time scale agree to within 50–100 years. Because changes at these two periods produce much of the distinctive character of rapid transitions in the SPECMAP $\delta^{18}O$ signal (Imbrie et al., 1992), the general visual similarity of the CO_2 and $\delta^{18}O$ trends results from the similar phasing at these periods. At the 100,000-year period, CO_2 leads SPECMAP $\delta^{18}O$ by 23° (6600 ± 2000 years).

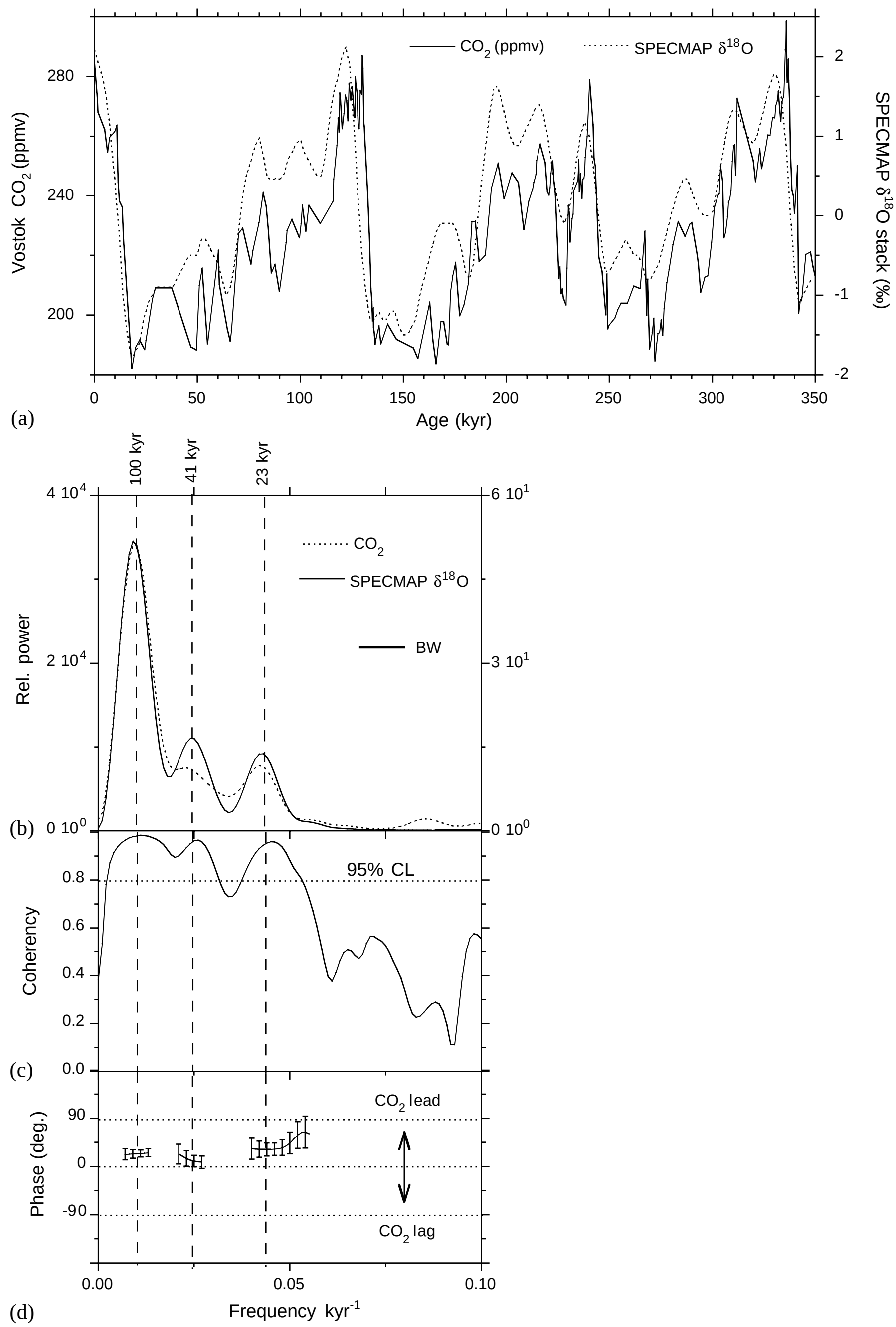

Fig. 5. Comparison of Vostok CO_2 (on the CH_4 time scale) and SPECMAP $\delta^{18}O$ (on the time scale of Imbrie et al., 1984). (a) Time series. (b–d) Cross-spectral analysis: (b) power spectra; (c) coherency between CH_4 and $\delta^{18}O$ signals; and (d) relative phasing at orbital periods. Spectral analysis followed Blackman–Tukey method, with 1/3 lags. Phases at the major orbital periods shown with 95% confidence intervals.

6. Discussion: Climatic role of CO_2 in ice-volume changes

One of the key issues in studies of orbital-scale climate change is the phasing between CO_2 and ice volume. Accurate definition of the relative phasing of these two signals should reveal critical cause-and-effect links in the climate system. The evidence above indicates that the CH_4 time scale for Vostok ice is sufficiently accurate to explore this issue. On the CH_4 time scale, Vostok CO_2 leads SPECMAP $\delta^{18}O$ at all three orbital periods (Fig. 5). Before this can be taken as evidence that CO_2 forces ice volume, however, two problems must be addressed.

The first problem is that, based on a wide array of evidence, the SPECMAP time scale is probably in error, giving ages for the $\delta^{18}O$ signal that average about 1500

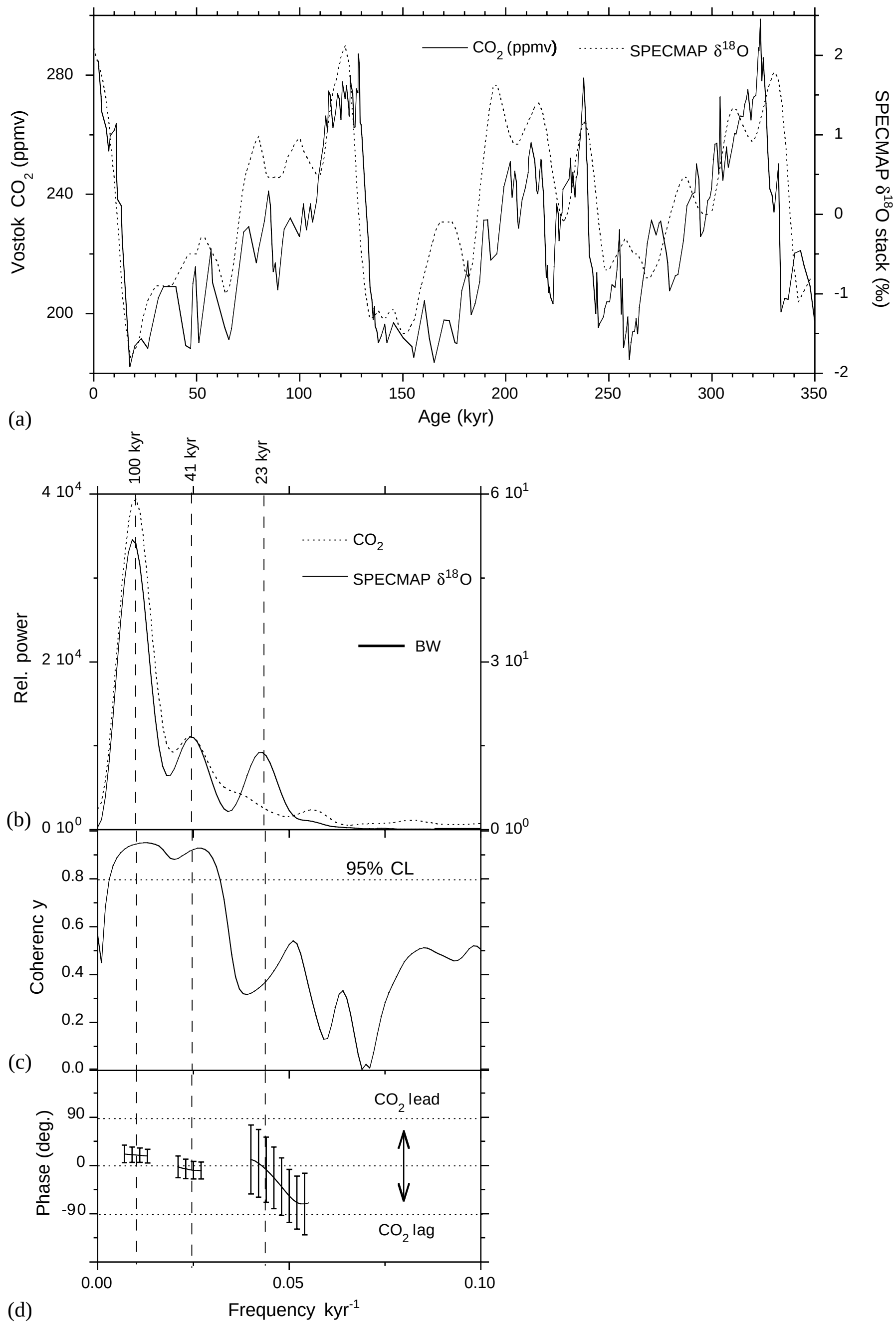

Fig. 6. Comparison of Vostok CO_2 (on the GT4 time scale) and SPECMAP $\delta^{18}O$ (on the time scale of Imbrie et al., 1984): (a) Time series; (b and d) Cross-spectral analysis: (b) power spectra; (c) coherency between CH_4 and $\delta^{18}O$ signals; and (d) relative phasing at orbital periods. Spectral analysis followed Blackman–Tukey method, with 1/3 lag. Phases at the major orbital periods shown with 95% confidence intervals.

years too young. Well-dated coral reefs provide a direct index of past ice-volume changes at some key isotopic transitions. By dating reefs formed at the end of termination II and during other high stands of sea level, Edwards et al. (1987) and Bard et al. (1990) found evidence for faster deglacial sea-level rises (ice-volume decreases) than implied by the SPECMAP $\delta^{18}O$ curve. Both concluded that coral-reef data indicate deglaciation some 3000 years earlier than the timing of the SPECMAP $\delta^{18}O$ signal across termination II.

A second line of evidence emerged from an attempt to tune the $\delta^{18}O$ signal using a different rationale. Pisias et al. (1990) allowed the lags of the 41,000-year and 23,000-year $\delta^{18}O$ responses behind the insolation forcing signals to vary through time in order to optimize matches of the resulting $\delta^{18}O$ signal to those observed in marine records. This approach contrasts with the constant phase lags assumed by SPECMAP in the tuning process (Imbrie et al., 1984). Pisias et al. (1990) found that on average the $\delta^{18}O$ signal was shifted earlier by 1500 years compared to the SPECMAP time scale. The largest offset from SPECMAP, 3500 years on termination II, agrees with the coral-reef dates.

A third line of evidence comes from an indirect comparison of the CH_4 time scale to the SPECMAP $\delta^{18}O$ time scale using the $\delta^{18}O_{atm}$ time scale of Shackleton (2000) as an intermediary. Shackleton (2000) reported that his $\delta^{18}O_{atm}$ time scale was on average 2000 years older (earlier) than that of SPECMAP, whereas we find that the CH_4 time scale averages 450 years younger than his $\delta^{18}O_{atm}$ time scale. Combining these results, the CH_4 time scale presented here is consistent with a 1550-year shift of the SPECMAP $\delta^{18}O$ time scale toward older (earlier) ages, as suggested by Pisias et al. (1990).

An array of evidence thus suggests that the SPECMAP $\delta^{18}O$ signal lags true ice volume by as much as 3000 years or more during rapid deglaciations and by an average of about 1500 years throughout the record. With the SPECMAP time scale adjusted by 1500 years toward older ages, the 1400-year CO_2 lead relative to SPECMAP $\delta^{18}O$ (and inferred ice volume) at the 41,000-year period disappears entirely, as does much of the 2000-year lead at the 23,000-year period. CO_2 retains a lead of 5000 years at the 100,000-year period of orbital eccentricity.

If CO_2 is nearly in phase with $\delta^{18}O$ (ice volume) at a given orbital period, it must be acting mainly as a positive (amplifying) feedback to the ice sheets, rather than as an independent source of forcing. This conclusion derives from the long time constant of ice-sheet responses (Weertman; 1964; Imbrie et al., 1984). Ice volume should lag thousands of years behind its primary source(s) of forcing. Ice sheets cannot be strongly forced by a CO_2 signal that has nearly the same phasing, except in the sense of receiving a self-amplifying positive feedback. The close phase relationship between CO_2 and $\delta^{18}O$ at the 41,000-year obliquity cycle is consistent with this kind of feedback relationship. In contrast, the CO_2 leads versus $\delta^{18}O$ at the 100,000-year cycles (and to a lesser extent the 23,000-year cycle) still permit an active forcing role for CO_2, if $\delta^{18}O$ is an accurate index of ice volume.

Unfortunately, marine $\delta^{18}O$ signals are not exact proxies for ice volume. The major complication is that marine $\delta^{18}O$ records also contain local temperature signals. Estimates of the fraction of marine $\delta^{18}O$ signals caused by temperature changes range from 1/3 (Shackleton, 1967) to 1/2 (Schrag et al., 1996), and the effect of the temperature overprints on $\delta^{18}O$ phasing is unclear (Mix et al., 2001). A second complication is that changes in $\delta^{18}O$ composition of ice sheets through time may produce offsets between marine $\delta^{18}O$ and ice volume (Mix and Ruddiman, 1984). As a result, the phasing of CO_2 with respect to the marine $\delta^{18}O$ signal does not necessarily indicate the phasing of CO_2 with respect to true ice volume.

Shackleton (2000) challenged the assumption that the 100,000-year component of $\delta^{18}O$ signals is an accurate record of ice volume. He found that half of the 100,000-year $\delta^{18}O$ signal in Pacific Ocean benthic foraminifera could be explained by changes in Pacific deep-water temperature, and the other half by ice volume. Within the sizeable errors of his multi-step analysis, the observed phase of the 100,000-year $\delta^{18}O$ signal in this core turned out to be partitioned into an early phased temperature component and a late ice-volume component.

The same problem complicates our attempt to compare the phasing of CO_2 against ice volume based on the SPECMAP $\delta^{18}O$ record. The average glacial-interglacial $\delta^{18}O$ amplitude of the cores used in the SPECMAP stack is 1.7‰ (Imbrie et al., 1984). If 0.9–1.3‰ of this total is caused by changes in ice volume (Schrag et al., 1996; Shackleton, 1967), a residual signal of between 0.4‰ and 0.8‰ remains, equivalent to an SST change of 1.7–3.3°C. Independent estimates of SST changes in the tropical and Southern Ocean cores from which the SPECMAP $\delta^{18}O$ stack was compiled are consistent with a temperature overprint of this size.

Because an SST overprint of 0.4–0.7‰ is larger than either the 23,000-year or 41,000-year components of the SPECMAP $\delta^{18}O$ signal, and amounts to half or more of the filtered 100,000-year $\delta^{18}O$ component (Imbrie et al., 1989), it could have a major effect on the phase of any or all of these $\delta^{18}O$ signals. SPECMAP concluded that SST leads $\delta^{18}O$ at all three orbital periods in the tropical and Southern Ocean region of the SPECMAP cores (Imbrie et al., 1992, 1993). As a result, any SST overprint in this region would probably be phased ahead of the $\delta^{18}O$ signals observed. If this is the case, the phase of the true ice-volume signal would have to lag behind $\delta^{18}O$ to balance the early SST overprint. This means that CO_2 is likely to lead ice volume by at least as much as it leads $\delta^{18}O$, and possibly by more.

Without a much more detailed analysis, the overprinting effect of SST on $\delta^{18}O$ at each orbital period cannot be deciphered. We can rule out the possibility that CO_2 lags behind ice volume at any of the orbital periods. But we cannot distinguish between the possibility that CO_2 leads ice volume, in which case it is an active part of the forcing of the ice sheets, or is in phase with ice volume, in which case it plays the role of an amplifying positive feedback to ice-volume changes.

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