we observed an erosion of $TiO_x$ at the center of the hole in excess of that observed with the planar $TiO_x$. In addition, the erosion of the carbon is higher than that expected, based on a planar sputtering yield of carbon by 2-keV Ar ions of one ejected atom per ion (7). Evolving holes are characterized by spatial variation of the surface composition, surface curvature, and slope, all of which are known to alter sputtering characteristics (8, 9). The ring is formed by either reduced erosion near the hole edge or by transport of material from the hole or surrounding area.

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# Sea-Surface Temperature from Coral Skeletal Strontium/Calcium Ratios


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**Seasonal records of tropical sea-surface temperature (SST) over the past $10^5$ years can be recovered from high-precision measurements of coral strontium/calcium ratios with the use of thermal ionization mass spectrometry. The temperature dependence of these ratios was calibrated with corals collected at SST recording stations and by $^{18}O/^{16}O$ thermometry. The results suggest that mean monthly SST may be determined with an apparent accuracy of better than 0.5°C. Measurements on a fossil coral indicate that 10,200 years ago mean annual SSTs near Vanuatu in the southwestern Pacific Ocean were about 5°C colder than today and that seasonal variations in SST were larger. These data suggest that tropical climate zones were compressed toward the equator during deglaciation.**


Retrieval of climatic data from the geologic record is important for validating climate models and for understanding the causes of past climate fluctuations. In most climate models, ocean temperature is a crucial parameter because of its linkage with other climate variables such as atmospheric moisture content and temperature, the extent of cloud cover and atmospheric albedo, or the patterns of oceanic and atmospheric circulation. Earlier efforts to recover past ocean temperatures from the geologic record have generally yielded inconsistent results or have proven to be difficult to apply. For example, attempts to recover ocean temperature from the O isotopic composition of biogenic marine carbonate sediments (*1, 2*) have been hampered because we do not know the history of fluctuations in the ocean water $^{18}O/^{16}O$ ratio, which varies as a function of the volume of the planetary ice caps, or, in the case of sea-surface water, can be modified by rainfall or evaporation effects. Efforts have also been made to reconstruct past ocean temperatures from the records of foraminiferal shell assemblages preserved in deep-sea sediments (3) based on knowledge of the temperature controls on modern foraminiferal assemblages (4). Such studies suggest that tropical SSTs were 0° to 2°C less than at present during the last glacial maximum (LGM) ~18,000 years ago (3). These findings, however, are at variance with estimates of SST based on the elevation of past mountain snow lines, which indicate that tropical SSTs were 3° to 6.5°C lower than at present during the LGM (*5–7*).

One promising method of recovering past SST records involves measuring the Sr/Ca ratios in corals (*8–10*). Scleractinian corals secrete skeletons composed of aragonite ($CaCO_3$), which incorporates both Sr and Ca into its structure. The ratio of incorporation of Sr to Ca is controlled by two factors: the Sr/Ca activity ratio of the ocean water, and the Sr/Ca distribution coefficient between aragonite and seawater (*11, 12*). This latter factor depends on the temperature of the seawater in which the coral grew but is only a weak function of the chemical composition of the seawater. Because of the long residence times of Sr and Ca in the oceans, it is probable that the seawater Sr/Ca ratio has remained essentially constant over time scales of about $10^5$ years. Thus, the Sr/Ca ratio of corals is a potential monitor of ocean temperature on these time scales. Earlier work confirmed that coral Sr/Ca ratios reflect SST to a precision of approximately ±3°C (2$\sigma$) (Fig. 1) (*8–10, 13*). However, this precision is about the same as the typical seasonal SST range observed in the tropics where scleractinian corals are found. Longer term variations in global average SST, such as the difference between mean SST for modern times and that at the LGM, may be even smaller than this, perhaps less than 2°C (3). Thus, this resolution is inadequate for evaluating seasonal or long-term ocean temperature variability.

In this paper we test the hypothesis that significantly better estimates of SST may be obtained from coral Sr/Ca ratios by improving the measurement precision of this elemental ratio. We first show that considerable improvement in the precision of Sr/Ca measurements can be obtained through use of thermal ionization mass spectrometry (TIMS). Next we assess whether improved analytical precision of this ratio translates into improved accuracy in SST. To do this, we correlated coral Sr/Ca ratios with ocean temperature by measuring $^{18}O/^{16}O$ ratios on the same coral samples, using the knowledge that coral $^{18}O/^{16}O$ ratios are a proxy for ocean temperature. Because our corals were collected from ocean island sites adjacent to SST recording stations, the accuracy of the Sr/Ca temperatures was independently assessed by comparison with actual SST measurements. Finally, we discuss the application of this method to recovery of SST from corals that grew during the last deglaciation.

Improved precision in the measurement of coral Sr/Ca ratios was made possible through use of isotope dilution with a triple $^{42}Ca$-$^{44}Ca$-$^{84}Sr$ spike in combination with TIMS (*14*). Both Ca and Sr were loaded


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together onto a double Re filament without prior chemical separation from the coral matrix. For a typical sample size of about 5 to 10 μg of Ca and 100 to 200 ng of Sr, we found that the average uncertainty (*15*) on the coral Sr/Ca ratio measured this way was ±0.02% (2σ) for an individual analysis. On the basis of four duplicate analyses of coral standard Tan-E, the external reproducibility (*15*) on the Sr/Ca ratio for typically sized samples is ±0.03% (2 SD). This precision is roughly two orders of magnitude better than obtained by earlier methods (Fig. 1) and translates into a possible analytical precision in temperature of ±0.05°C (2σ) based on the Sr/Ca and temperature relation shown by Smith *et al.* (*9*). With this greater degree of analytical precision, the remaining issue becomes the accuracy with which the coral Sr/Ca ratio reflects ocean temperature.

For the coral species *Porites lobata*, we recalibrated the Sr/Ca thermometer using the relation between coral Sr/Ca and $^{18}O/^{16}O$ ratios, using $^{18}O/^{16}O$ ratios as a proxy for SST (*16*, *17*). We collected annually banded corals for calibration from ocean islands in the western and central Pacific. Corals were recovered from barrier reefs that were well washed with seawater from the open ocean to ensure that they grew under conditions representative of the open ocean and not of closed lagoons, which could have anomalous seawater Sr/Ca or $^{18}O/^{16}O$ ratios. Fluctuations in salinity were insignificant at these sites as determined from daily salinity records, confirming that these reefs were exposed to open ocean conditions. Corals from Noumea, New Caledonia, and Papeete, Tahiti, were sampled parallel to the growth direction in time series with temporal resolution of approximately monthly intervals. We obtained both $\delta^{18}O$ (*18*) and Sr/Ca analyses from the same samples of coral by first extracting the oxygen (*19*) at 80°C by phosphoric acid dissolution in a quartz extraction line. The Sr and Ca concentrations were then obtained from TIMS analysis of the remaining residue.

For the New Caledonia site, both $\delta^{18}O$ and the Sr/Ca ratio vary cyclically with an annual periodicity and are strongly correlated (Fig. 2), yielding a temperature calibration (*20*) of the coral Sr/Ca ratio for the species *P. lobata*:

$$T\ (^{\circ}C) = 171.6 - 16013 \times (Sr/Ca)_{atomic} \qquad (1)$$

Within error, this relation is similar to that derived by Smith *et al.* (*9*) for the genus *Porites* but has a slightly different slope and intercept, as well as improved precision (Fig. 1).

Using Eq. 1, we compared the calculated Sr/Ca temperatures with the actual SST recorded at New Caledonia and Tahiti (Figs. 3 and 4) as a test of the accuracy of the Sr/Ca thermometer. Matching of the Sr/Ca temperature and SST records was enabled by approximately superimposing the annual maxima in each record and assuming a constant coral growth rate throughout the year. For the Tahiti coral, the average difference between Sr/Ca temperature and actual 10-day average SST is 0.34°C. Thus, the resulting correspondence between the calibrated Sr/Ca temperatures and actual SST indicates that the Sr/Ca thermometer is both accurate and robust for at least these two quite different sites. These data suggest that coral Sr/Ca ratios are indeed a proxy for SST.

In order to obtain paleotemperatures from Sr/Ca ratios of ancient corals, we must assume that variations in the ocean Sr/Ca ratio have been small over the time period of interest. Because of the long ocean residence times of Sr and Ca [$5.1 \times 10^6$ years for Sr and $1.1 \times 10^6$ years for Ca (*21*)] relative to ocean mixing times (~1000 years), temporal and geographic variations of Sr/Ca ratios in the open ocean are small

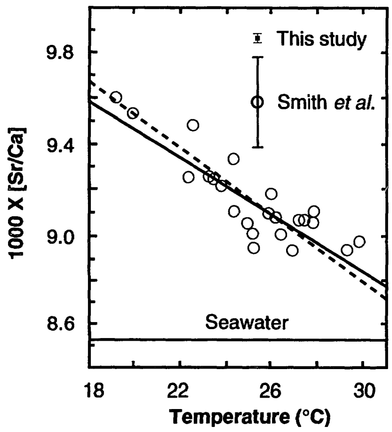


**Fig. 1.** Plot of Sr/Ca ratios in scleractinian corals against the temperature of the seawater from which they grew. The work of Smith *et al.* (*9*) is shown by open circles and the dashed line. Results of our work (solid line) indicate that some improvement in this correlation is possible, although the slope and intercept of the resultant linear relation (solid line) are similar to those determined in (*9*). The error bar for Smith *et al.* is the average (2σ) error. The error bar for our work is ten times the average (2σ) error.

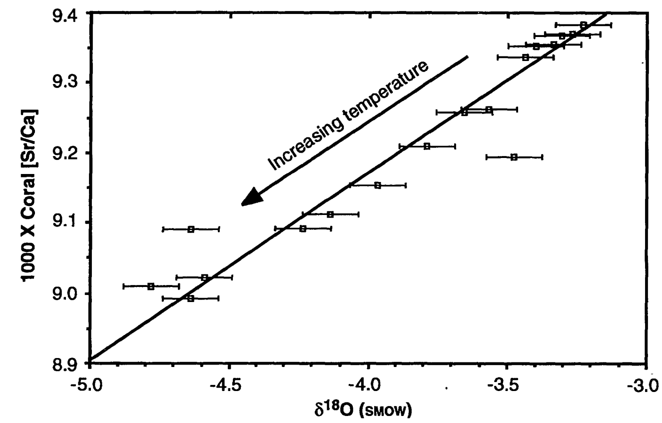


**Fig. 2.** Sr/Ca ratios versus $\delta^{18}O$ values from the same samples of coral. Horizontal error bars are the average (2σ) external analytical error on the $^{18}O/^{16}O$ ratio. Vertical error bars (height of the open square) are the average (2σ) external analytical errors in the Sr/Ca ratio. External errors include uncertainties from the sample extraction process and are based on repeated analysis of carbonate standards (*19*).

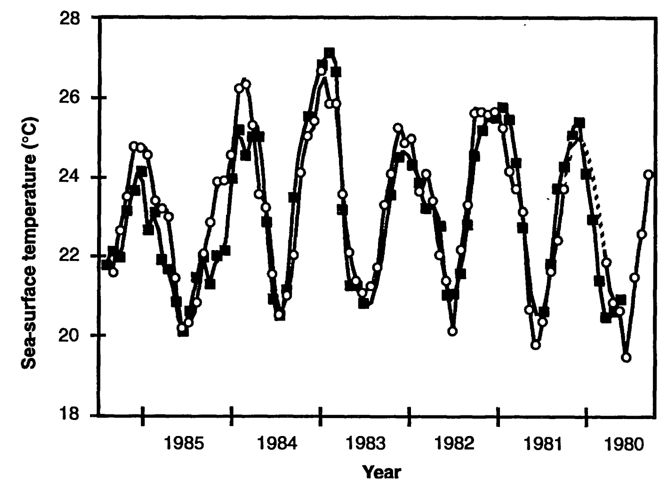


**Fig. 3.** Comparison between actual SST (open circles) recorded at the temperature-recording station at Amedee Lighthouse, Noumea, New Caledonia, and Sr/Ca temperatures (filled squares) for samples of the coral species *P. lobata*, using Eq. 1. Actual SST data points represent 30-day averages of daily SST measurements. The coral sample size used for Sr/Ca analyses represents approximately monthly intervals of growth. As such, coral Sr/Ca temperatures represent the average ocean conditions over these intervals. The dashed portion of the temperature record represents a period for which SST records were not available.

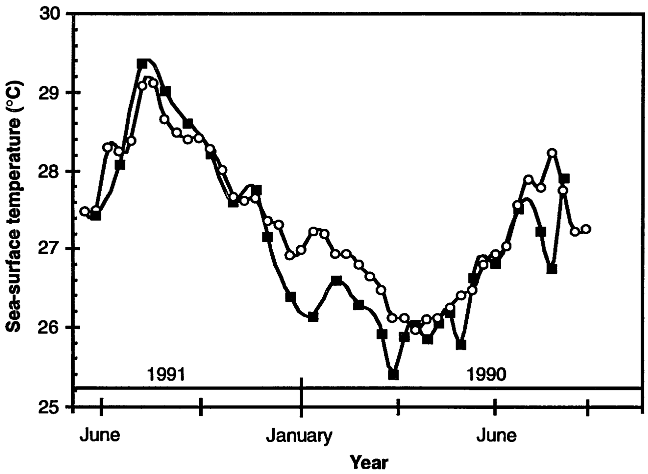


**Fig. 4.** Comparison between actual SST (open circles) recorded at the temperature recording station at Papeete, Tahiti, and Sr/Ca temperatures (filled squares) for samples of the coral species *P. lobata*, using Eq. 1. Actual SST data points represent 10-day averages of daily SST. Coral Sr/Ca temperatures represent the average ocean conditions over approximately 10-day intervals. The average difference between Sr/Ca temperature and the actual 10-day average SST is 0.34°C.

(*8, 22*), although the modern oceans do appear to show variations outside of analytical uncertainty (*23, 24*). Consequently, for time scales on the order of $10^5$ years, only small shifts in the ocean Sr/Ca ratio would generally be expected as a result of variations in river-water flux. Perturbations in the calcite compensation depth (CCD) (*25*) associated with Quaternary climate shifts could potentially cause more rapid changes in ocean Sr/Ca ratios. If such changes resulted in a 10% change in the area of sea floor suitable for calcite deposition, this would result in a maximum shift in the seawater Sr/Ca ratio of about 0.45% between glacial and interglacial periods, provided such CCD excursions did not cause wholesale dissolution of calcite sediments already on the sea floor. Errors in temperature introduced by uncertainties in the oceanic Sr/Ca ratio of this magnitude are less than about 0.5°C, which is about the same as the uncertainty of the Sr/Ca thermometer. In principle, this permits the recovery of paleo-SST records from corals that grew in the last $10^5$ years.

Fossil *P. lobata* corals that grew during the last deglaciation have been recovered from drilling into a paleoreef on the island of Espiritu Santo, Vanuatu, in the southwestern Pacific (168°E, 16°S). We used one of these to reconstruct a 4.5-year-long paleo-SST record based on the coral Sr/Ca ratio (Fig. 5). An adjacent coral in the drill core was radiocarbon dated (*26*) at 10,160 ± 200 ($2\sigma$) years before present. The coral Sr/Ca record fluctuates cyclically with an annual periodicity as evidenced by the spacing of the annual bands seen on an x-radiograph of this coral. Over this 4.5-year period the mean annual SST was 21°C and the average seasonal temperature range was 4.5°C. These conditions are dramatically different from those found at this site today (*27*), a mean annual SST averaging ~26.5°C with a mean seasonal temperature range of 3°C. Indeed, such conditions are much more similar to those currently seen in southern New Caledonia, 5° of latitude south of Espiritu Santo (see Fig. 3). This result suggests that the belt of tropical climate conditions may have been compressed toward the equator ~10,200 years ago. These findings are somewhat surprising when compared with the CLIMAP (Climate: Long-Range Investigation, Mapping, and Prediction) climate reconstructions (*3*) for the LGM ~18,000 years ago, which suggest that SST in this area was then approximately the same as modern values. If the CLIMAP reconstructions and the Sr/Ca data are taken at face value, tropical SSTs must have decreased dramatically in this region during the deglaciation before rising to their present values (*28*). On the other hand, if the inference from depression of snow lines (*5–7*) and the Sr/Ca data are taken at face value, tropical SSTs appear to have been low during the LGM and may have remained low at least halfway through the last deglaciation before rising to their present values. The latter is a simpler conclusion. However, because the Sr/Ca data are limited, we cannot rule out the possibility that our data represent a regional phenomenon or a short-term deviation from general climate trends, perhaps related to the Younger Dryas event (*29*). The use of high-precision $^{230}$Th methods for dating corals (*30*) from this and other sites may make it possible to decide between these possibilities.

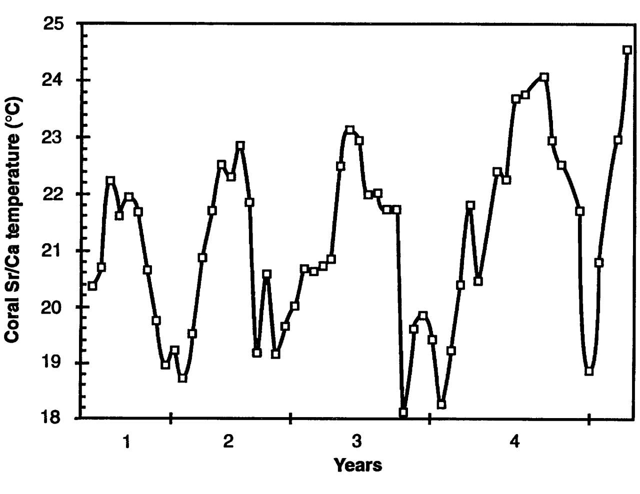


**Fig. 5.** A 4.5-year temperature record obtained from a fossil *P. lobata* recovered from drilling into a paleoreef on the island of Espiritu Santo (Vanuatu) in the southwestern Pacific (168°E, 16°S). This coral has been assigned an age of 10,160 ± 200 ($2\sigma$) years before present (*26*).

In addition to its use as an ocean thermometer, the correlation observed between coral Sr/Ca ratios and $\delta^{18}O$ may also make it possible to determine sea-surface $\delta^{18}O$ by removal of the temperature component of the coral $\delta^{18}O$ signal. Maps of sea-surface $\delta^{18}O$ generated in this way might be used to estimate variations in the volume of the planetary ice caps or to generate maps of sea-surface salinity (*31, 32*). The latter might in principle be used to recover past patterns of rainfall and evaporation over the tropical oceans. Finally, heavy rainfall events can result in short-term (week-long to month-long) depletions in surface-ocean water $\delta^{18}O$. Such events may cause deviations from the observed linear relation between Sr/Ca ratio and $\delta^{18}O$. If so, it may be possible to assess the frequency of past tropical storm events from time-series analysis of high-resolution coral Sr/Ca ratios and $\delta^{18}O$ records. Possible nonequilibrium fractionation of the O isotopes (*17*) in corals, however, may limit recovery of information about such rainfall or ice-volume variations.

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11. A distribution coefficient is usually defined by an equation of the form: $D_{Sr}$ = $(Sr/Ca)_{mineral}/(Sr/Ca)_{fluid}$, where $(Sr/Ca)_{mineral}$ and $(Sr/Ca)_{fluid}$ are the molar concentration ratios of these elements in the mineral and fluid, respectively.
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14. Sr and Ca concentrations were measured by isotope dilution on a Finnigan MAT 262 solid source mass spectrometer, using static Faraday collection. An exponential mass fractionation (*33*) correction for $^{84}Sr/^{86}Sr$ and $^{44}Ca/^{42}Ca$ was used, correcting to an assumed (*34*) natural $^{86}Sr/^{88}Sr$ = 0.1194 and an assumed (*33*) natural $^{42}Ca/^{44}Ca$ = 0.31221. Spike isotopic composition corrections were based on gravimetric determinations for Ca, and on non–fractionation-corrected TIMS determinations of the isotopic composition of the Sr spike. Results of 19 runs of Minnesota Isotope Laboratory standard ISC-1 Ca yielded an average $^{40}Ca/^{42}Ca$ = 151.030 ± 19 (2σ), whereas results of 10 runs of National Bureau of Standards (NBS) standard 987 Sr yielded an average $^{87}Sr/^{86}Sr$ = 0.710239 ± 10 (2σ).
15. Each Sr or Ca analysis constitutes between 50 and 100 individual mass spectrometric scans (isotopic ratios). A standard error (SE) of the mean is calculated for each analysis; these SEs are in turn propagated to determine the SE for the Sr/Ca ratio. "Average uncertainty" in the sense used here refers to the average (2σ) SE for all of the Sr/Ca analyses reported in this paper. "External reproducibility" as it is used here refers to two standard deviations of the population, where the population constitutes the mean values of several different determinations of the Sr/Ca ratio of a standard.
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18. $\delta^{18}O$ is the normalized deviation, in parts per thousand, of the sample $^{18}O/^{16}O$ relative to standard mean ocean water (SMOW) (*35*).
19. We performed $\delta^{18}O$ analyses on a Finnigan MAT delta-E mass spectrometer. Average internal precision on the $\delta^{18}O$ analyses is reported at 0.07 per mil (2σ) on a typical 5-mg sample of coral. Five runs of standard NBS 18 yielded an average $\delta^{18}O$ (SMOW) = 7.18 ± 0.06 per mil (2σ), whereas results of nine runs of standard NBS 19 yielded somewhat poorer external reproducibility, with an average $\delta^{18}O$ (SMOW) = 28.75 ± 0.10 per mil (2σ).
20. The Sr/Ca temperature calibration made use of the $\delta^{18}O$ versus temperature calibration for the coral genus *Porites* generated by McConnaughey (*17*). This equation may be expressed as: $\delta^{18}O_c - \delta^{18}O_w = 0.594 - 0.209\,T$(°C), where $\delta^{18}O_c$ and $\delta^{18}O_w$ are the O isotopic compositions of the coral and seawater, respectively. The value of $\delta^{18}O_w$ for one seawater sample from the Amedee Lighthouse, Noumea, New Caledonia, calibration site was +0.52 ± 0.06 per mil (2σ). Average seawater $\delta^{18}O$ was assumed to be +0.6 per mil for this site based on published compilations.
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36. We are grateful to G. Shen for stimulating us to pursue improvements in the coral Sr/Ca ocean thermometer. We also thank T. Crowley, T. Quinn, C. Gallup, and R. Schultz for helpful comments. This work was made possible by the following National Science Foundation grants: EAR-8917103 (J.W.B. and W.E. Seyfried, Jr.), EAR-8904895 (R.L.E.), EAR-8904705 (R.L.E.), ATM-8921760 (R.L.E.), EAR-8904987 (F.W.T.), ATM-8904987 (F.W.T.), and EAR-9004762 (E.I.). Support for the TIMS analytical facility was made possible by NSF grant EAR-8817260 (R.L.E.), as well as funds from the University of Minnesota.

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# Maintenance of Strong Rotational Winds in Venus' Middle Atmosphere by Thermal Tides

Matthew Newman* and Conway Leovy

**The cloud-level atmosphere of Venus takes little more than 4 days to complete one rotation, whereas the solid planet below has a 243-day period. Computer simulations of the circulation of the Venus middle atmosphere between 40 and 85 kilometers, as driven by solar radiation absorbed in the clouds, reproduce (i) the observed cloud-level rotation rate, (ii) strong vertical shears above and below the cloud tops, and (iii) midlatitude jets and strong poleward flow on the day side. Simulated circulations converge to yield nearly the same zonal winds when initialized with both stronger or weaker rotation rates. These results support the hypothesis that the observed cloud-top rotation rate is maintained by statistical balance between fluxes of momentum by thermal tides and momentum advection by mean meridional circulation.**

Virtually the entire Venus atmosphere, from above the lowest scale height to well above the cloud tops (65 to 70 km), rotates much faster than the solid planet. Although the equatorial rotational speed of the solid surface is only 4 m $s^{-1}$, the atmospheric rotational speed reaches a maximum of approximately 100 m $s^{-1}$ near the equatorial cloud-top level (65 to 70 km) (*1*). This phenomenon, known as superrotation, is the central dynamical problem of the Venus atmosphere. We report here the results of numerical simulations aimed at clarifying the mechanism for maintaining the equatorial cloud-top rotation.

Although the zonally symmetric Hadley circulation, which is thermally driven, can carry angular momentum upward, it transports this angular momentum to high latitudes and cannot maintain a maximum in equatorial angular momentum near cloud-top level. Waves are needed to counter this transport, as well as friction (*2*). Planetary waves arising from horizontal shear instability of the zonal flow (barotropic instability) could maintain the equatorial rotation by transporting angular momentum horizontally from midlatitudes toward the equator, but only if wave amplitudes are sufficiently large (*3*). Observational evidence for the required transport of eddy momentum by large amplitude planetary waves is lacking, however (*4*).

Alternatively, vertically propagating waves could provide the required momentum source. The relative motion between the rotating atmosphere and the pattern of solar heating, which has a maximum where solar radiation is absorbed in the cloud tops, drives diurnal and semidiurnal thermal tides that propagate vertically away from the cloud-top level. The effect of this wave propagation is to transport momentum vertically toward the cloud-top level at low latitudes and accelerate the mean zonal flow there. At higher altitudes, where much of the energy of the thermal tides is dissipated, these waves decelerate the mean zonal flow (*5–7*). We investigated the tidal mechanism using a numerical model that includes the zonally symmetric components of the flow and the two longest zonal waves. This model also allows us to address several outstanding problems posed by observations of Venus' middle atmosphere: (i) observed temperature distributions indicate that there are strong cyclostrophically bal-

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