the "zipper" model predicts that the resulting change in kink density along the ledge will, after a time, give rise to three regions in the pit: region a, the old ledge not yet reached by the new kink density; region b, the ledge originally formed by kinks initiated at the old rate but which has since been traversed by kinks initiated at the new rate; and region c, the new ledge formed after the change in the kink initiation rate.

The mechanism indicates that pit regions a and c will have constant slope (ledge-spacing) and will move outward at a constant rate [dx/dt or dx''/dt, see the pit diagram (Fig. 2A)] equal to the ledge velocity, v_ℓ or v_ℓ'. However, region b, which is unique to the zipper mechanism, will move outward more rapidly, with a rate dependent upon the kink velocity v_k along the ledge. One can calculate the characteristics of region b on the assumption that the only effect that an impurity would have on triangular pits is a discontinuous change in r_k. (In this model we neglect small changes in pit shape caused by a change in r_k.) The outer edge of region b (at a distance x' from the pit center) will move at a decreasing rate because the time, $\delta t = 6\sqrt{3}\, x'/v_k$, required for a kink to make one trip around the pit increases farther out from the pit center:

$$\frac{dx'}{dt} = \frac{\lambda\, v_k}{6\sqrt{3}\, x'} \qquad (1)$$

where λ is the original, region a, ledge spacing. The ledge spacing λ' at the outer edge of region b will be

$$\lambda' = \lambda + \frac{\sqrt{3}\, x'\, (v_\ell - v_\ell')}{v_k} \qquad (2)$$

Thus, the zipper mechanism implies that impurity perturbations lead to pit regions of variable slope which sweep out at velocities greater than the ledge velocities. This is observed upon vaporization of arsenic crystals. Measurements of the rate of growth of regions a, b, and c, as illustrated in Fig. 2, are in accord with the model presented in the preceding paragraph. For typical triangular pits, $dx/dt = v_\ell = 5 \times 10^{-7}$ cm sec^{-1} at 566 K. This corresponds to a kink initiation rate of $r_k = v_\ell/d_k = 8$ kinks per second per dislocation, where d_k is the distance a ledge moves when a kink passes a given point. The vaporization rate at 566 K is 1×10^{14} molecule cm^{-2} sec^{-1} (*4*). The kink velocity v_k can be computed from the slope of a plot of $(x')^2$ as a function of time for region b, such as that in Fig. 2, via Eq. 1. At 566 K, $v_k = 0.3$ cm sec^{-1}. From this we calculate that the rate at which As_4 units are released from a kink is 7×10^6 molecules per second per kink and that the average length of the spiral ledge between kinks is 3×10^6 Å.

The zipper mechanism further implies that, if the rate of kink initiation is increased markedly, $v_\ell' > v_\ell$, then, at some distance x'_{lim} from the pit center, $\lambda' = 0$ in Eq. 2. At x'_{lim}, ledges pile up and the pit will bore a hole through the crystal, because ledges moving at the original rate are caught by ledges moving at the increased rate before the kinks have time to traverse the circumference of the pit. This is observed when arsenic vaporization is catalyzed by dissolved oxygen or neutron bombardment (Fig. 3). Assuming that catalysis causes v_ℓ' to be equal to $9v_\ell$ in deep pits (*6*), we compute $x'_{lim} = 1 \times 10^{-3}$ cm from the numbers above, a result in agreement with the observed dimensions of deep pits. It appears that many of the features of arsenic vaporization catalysis (*6*) can be explained if catalysis involves vacancy diffusion to dislocation cores, where the vacancies increase the rate of kink initiation five- to tenfold.

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Laurentide Ice Sheet Meltwater Recorded in Gulf of Mexico Deep-Sea Cores

Abstract. *Oxygen isotopic measurements in three Late Quaternary deep-sea cores from the Gulf of Mexico record a major anomaly between about 15,000 and 12,000 years ago superimposed on a more characteristic oceanic oxygen isotopic curve. This resulted from major influx of isotopically light glacial meltwater via the Mississippi River from the disintegrating Late Wisconsin Laurentide Ice Sheet 2000 kilometers to the north.*

During the last 2.6 million years the northern North American continent has been periodically covered by immense ice sheets (*1*). The Laurentide Ice Sheet advanced to its Late Wisconsin maximum about 18,000 years ago (*2*), at which time it covered an area of about 13×10^6 km^2, similar in dimensions to that of the present-day Antarctic Ice Sheet (*3*). After about 18,000 years ago this last ice sheet began to shrink, reaching approximately 30 percent of its maximum size about 12,000 years ago with considerable areas uncovered in former south and southwest sectors (*3*). Until now the retreat of this ice cap is known almost entirely by radiocarbon dating of materials associated with the glacial retreat across North America (*2, 4–6*). We present a history of the melting of the southern Laurentide Ice Sheet between about 18,000 and 11,000 years ago based on oxygen isotopic analyses of planktonic foraminiferans in the upper parts of three Late Quaternary deep-sea cores (*7*) from the western Gulf of Mexico (Fig. 1), ranging in

depth from 2462 to 3408 m (*8, 9*). These cores have high sedimentation rates, ranging from 7 to 27 cm per 1000 years (*10*), and abundant planktonic foraminiferal assemblages, and are thus valuable for high-resolution paleoclimatic studies (*9, 11*).

The melting of large ice sheets can be studied by utilizing changes in the ratio of ^{18}O to ^{16}O (*12*) in the sedimentary record because fresh water derived from melting ice is relatively impoverished in ^{18}O. Thus marine waters diluted by glacial meltwater are isotopically more negative than undiluted oceanic waters. The isotopic record in Mediterranean deep-sea cores (*13*) has been interpreted in terms of episodic major outflow of fresh water from the Black Sea into the Mediterranean (*14*).

Oxygen isotopic analyses have been made of the planktonic foraminiferan *Globigerinoides sacculifer* at 10- to 20-cm intervals in core K 97 and 10- to 50-cm intervals in cores K 120 and K 139 (*15*). In K 97 a sedimentation rate of 27 cm per 1000 years provides a resolution of 370 ± 30 years at a sampling interval of 10 cm.

The salient feature of the oxygen isotopic record in the three cores (Fig. 2) is a major anomaly near the end of the last glaciation, with $\delta^{18}O$ reaching −2.1 to −2.6 per mil, superimposed on a more characteristic latest Quaternary marine isotopic record (*16*). In Fig. 2 the oxygen isotopic record is compared with a planktonic foraminiferal biostratigraphic subzonation established for the Gulf of Mexico (*9*), which enables detailed correlations between the three cores. The isotopic anomaly clearly occurs within subzone Y1. As no direct age determinations are yet available for these cores, we have dated the isotopic record by extrapolation, using sedimentation rates based on the Z-Y zonal boundary (Fig. 2), which is radiocarbon-dated at 11,000 ± ~500 years in the Caribbean and Gulf of Mexico (*17, 18*). The Z-Y boundary by definition (*18*) is based on the first consistent occurrence of the *Globorotalia menardii* plexus (*G. menardii* and *G. menardii tumida*) (*19*).

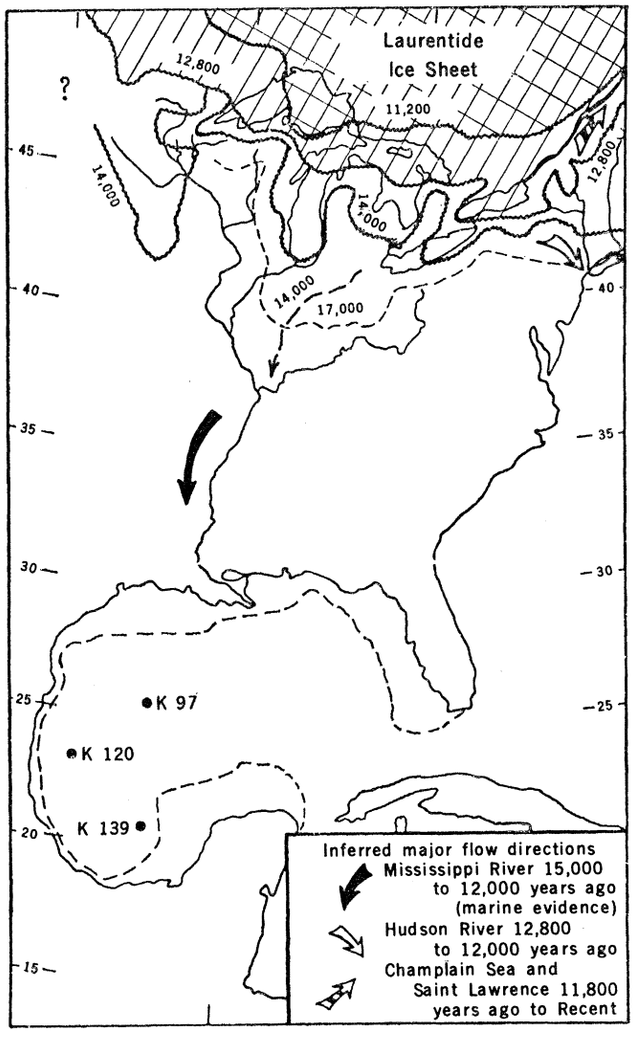

Fig. 1. Map of eastern North America and the Gulf of Mexico showing the locations of the cores studied, four successive positions of the southern margin of the melting Laurentide Ice Sheet between 17,000 and 11,200 years ago (*4*), and inferred major glacial meltwater flow directions (arrows), which changed as the ice sheet disintegrated. The nature of the flow toward the east of North America is based on continental evidence (*5*). The present-day 80-m water depth contour (*28*) (dashed line in Gulf) approximates the position of sea level 16,000 years ago (*26*) and demonstrates the reduced size of the Gulf of Mexico during the last glacial episode.

Although the isotopic anomaly is clearly recorded in all the cores analyzed, its definition is clearest in K 97 because of that core's considerably higher sedimentation rate and closer sampling; therefore we base the chronology only on K 97 (Fig. 2). Assuming that the 11,000-year datum is correct and that sedimentation rates are constant over subzones Z1, Z2, Y1, and Y2, isotopic values begin to become substantially more negative about 17,000 years ago, with the most negative values about 13,500 years ago. This was followed by a rapid return to more characteristic oceanic isotopic values by about 11,500 years ago.

We interpret this isotopic anomaly as representing the massive inpouring of glacial meltwater into the Gulf of Mexico via the Mississippi River system during the early melting phases of the late Wisconsin Laurentide Ice Sheet. At the time of maximum inpouring of this water, surface salinities were evidently reduced by about 10 percent or 2 or 3 per mil throughout at least the entire western Gulf of Mexico. The isotopic change is far too large to have been caused by temperature increase (it would represent an unlikely rise of some 8°, to 33°C), and there is no evidence from other regions for anomalously high temperatures at this time, nor do the associated planktonic foraminiferal faunas indicate such a temperature increase (*9*). Such a salinity decrease should primarily affect the surface waters of the Gulf, and hence planktonic foraminiferans secreting their shells at greater water depths (*20*) should record a smaller salinity effect on isotopic composition. To test this, four planktonic species, two surface-dwelling and two from deeper water, were analyzed from the peak of the anomaly (section at 370 cm in K 97) and from a typical Holocene level (197 cm in K 97). *Globigerinoides ruber* and *G. sacculifer* are, respectively, 1.50 and 1.60 per mil more isotopically negative at the inferred peak of meltwater inflow. By contrast, the deeper-dwelling *Neogloboquadrina dutertrei* and *Globorotalia truncatulinoides* are only 0.32 and 0.33 per mil more negative. In the absence of the glacial meltwater anomaly, all species would be expected to be more than 1

per mil more positive 14,000 years ago (*16*). If the inflowing meltwater had an isotopic composition of about −30 per mil (*21*), these figures suggest a dilution of more than 8 percent for surface water and more than 4 percent for deeper water.

Our Holocene values (*22*) are very similar to those obtained by Emiliani (*23*) and imply a depth habitat near 100 m for *N. dutertrei* and below 200 m for *G. truncatulinoides*. If we assume that these species occupied the same depths during the glacial meltwater phase, we infer a salinity of about 33 per mil at the surface and about 34.5 per mil below 100 m. This can be compared with present-day salinities of about 36 to 36.5 per mil in the western Gulf of Mexico. The planktonic foraminiferal faunas appear to have been little affected by this salinity stratification (*9*); the increase in relative frequency of *N. dutertrei*, which prefers lower salinities (*24*), is a possible response, although this is difficult to prove since both increased $CaCO_3$ dissolution and rising temperature also lead to an increase in its relative frequency.

A major effect of glacial meltwaters on the salinities of the Gulf of Mexico near the end of the last glaciation might be expected because immense amounts of meltwater produced by the ice sheet initially drained southward via the Mississippi River system rather than eastward; this was due to the configuration of the ice sheet itself and to the isostatic depression of northern North America that resulted from the weight of the ice sheet (*5*). Furthermore, large ancient river channels associated with the Mississippi River system represent direct evidence of substantial southward meltwater transport into the Gulf (*25*). Meltwaters entering the Gulf between about 16,000 and 12,000 years ago would probably have had a greater effect on surface salinities because the lowered sea level at that time exposed much of the continental shelves, reducing the size of the Gulf (*26*) (Fig. 1).

The isotopic fluctuations indirectly dated in K 97 therefore provide a history of meltwater flow southward from the disintegrating Laurentide Ice Sheet in its early phases. Our marine evidence shows that the last melting of the Laurentide Ice Sheet commenced about 17,000 years ago (Fig. 1), with almost all meltwater from the southern margin flowing southward into the Gulf (*4*). This agrees with the continental glacial evidence that indicates maximum southward extension of the Late Wisconsin Ice Sheet between 17,000 and 18,000 years ago (*2, 3*) (Fig. 1). After this, meltwater discharge into the Gulf steadily increased in volume, reaching a peak approximately 13,500 years ago. This was followed by a rapid decline in meltwater discharge, with normal marine isotopic composition being restored by 11,500 years ago. Since 11,500 years ago freshwater discharge into the Gulf has been negligible. The rapid decline in southward discharge between 13,500 and 11,500 years ago does not reflect a decrease in the rate of disintegration of the ice sheet, which was still about 60 percent of its maximum size (*3*), but represents a major change in the direction of meltwater flow from southward to eastward. The marine evidence suggests that this change commenced about 13,000 years ago, with dominant eastward flow developing by about 11,500 years ago. Continental evidence indicates that important discharge via the Hudson River occurred between 12,800 and 12,000 years ago (*5*) (Fig. 1), partially tapping the southward flow. This event appears to be recorded in the isotopic record of the Gulf by decreasing negative values between 13,500 and 12,000 years ago. Further northward retreat of the ice sheet uncovered the area of the present-day Gulf of Saint Lawrence by 11,800 years ago, allowing eastward flow of almost all meltwaters from the melting ice sheet (*5*). This discharge was initially into the Champlain Sea. About this time, meltwater flow also commenced through the Fosmill Notch northeast of Lake Huron, tapping large marginal proglacial lakes to the southwest of the ice sheet (*27*). These events in combination essentially prevented any further important southward discharge. Based on our chronology, southward flow of meltwater inferred to have occurred from Lake Agassiz (west of the ice sheet) at various intervals between 12,000 and 10,000 years ago and even as recently as 8500 years ago (*5*) are not recorded in the marine record and may not have been large enough to effect surface salinities. On the other hand, it is possible that short-term meltwater events that may have occurred during the Holocene will be revealed by more detailed future analyses.

Our investigation thus shows that in certain oceanic regions there is a record of the history of discharge of glacial meltwaters from continental ice sheets. Earlier meltwater phases almost certainly would have influenced salinities in the Gulf of Mexico and will

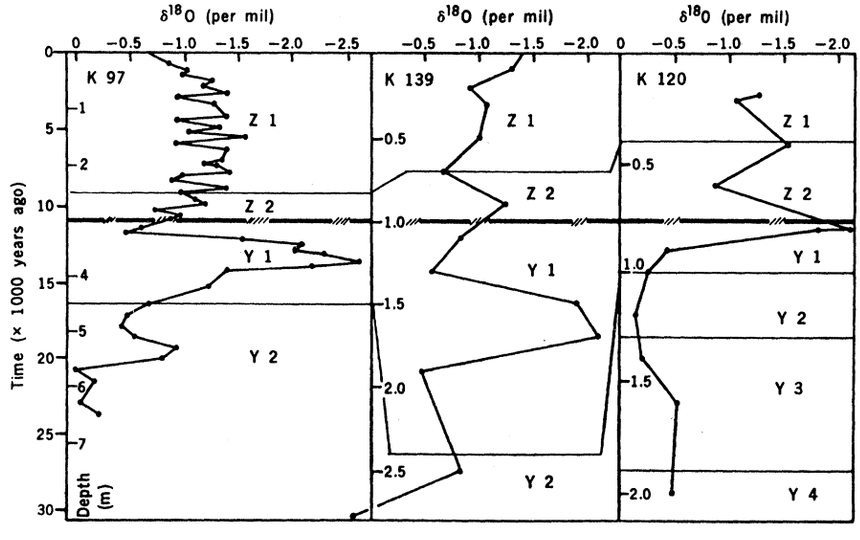

Fig. 2. Oxygen isotopic data for *Globigerinoides sacculifer* in three Late Quaternary cores; $\delta^{18}O$ is the per mil deviation with respect to PDB1 (*12*). Core K 97, which has a very high sedimentation rate (27 cm per 1000 years) is calibrated to a chronology (scale at extreme left) established by assuming an age of 11,000 ± ~ 500 years ago for the Z-Y paleontological boundary (heavy broken line) and a constant sedimentation rate. Differences between curves in relation to chronology are attributed to large differences in sedimentation rates between cores (*10*). Depth in meters is shown for each core. Planktonic foraminiferal subzones (Z1, Z2, Y1, and Y2) are correlated between cores (*9*). An oxygen isotopic anomaly is clearly shown in the Y1 subzone.

provide information on the extent of earlier ice sheets, since it can be assumed that no substantial meltwaters would have entered the Gulf unless the southward extent of the ice sheet was greater than the latest Wisconsin limit about 11,200 years ago (Fig. 1). Such an approach will be of particular value since little is known about earlier episodes of deglaciation, because succeeding glacial advances have redistributed the older deposits.

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$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)\text{sample}}{(^{18}O/^{16}O)\text{PDB1}} - 1\right] \times 10^{3}$$

where PDB is the standard Pee Dee Belemnite. For means of calibration, see N. J. Shackleton, *Colloq. Int. Cent. Natl. Rech. Sci.* **219**, 203 (1974).
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Submarine Barite-Opal Rocks of Hydrothermal Origin

Abstract. *Unusual submarine rocks consisting of barite, opal, and volcanic detritus were recovered from the Lau Basin northeast of Australia. It is proposed that these rocks were formed when hydrothermal solutions emanating from a fracture zone offsetting the active spreading center in the Lau Basin came into contact with cooler ocean waters.*

Submarine barite-opal volcanic rocks were recovered from the Lau Basin, a marginal basin located northeast of Australia. The rocks were obtained by dredge from atop the Peggy Ridge, presently believed to be a fracture zone offsetting the active spreading center in the Lau Basin. The spreading center generally trends northeast-southwest dividing the Lau and Tonga ridges (*1*). The whole basin is less than 10 to 15 million years old, and the sediment cover is sparse, occurring in linear, probably fault-controlled troughs (*2*). Barite-opal rocks of this young age are not common in the marine environment and their origin is considered in this report.

Dredge hauls from the Peggy Ridge in the Lau Basin consist of ocean ridge type tholeiitic basalts exhibiting various degrees of weathering, together with pumice from the Tonga and Lau ridges. In only one dredge, 7 TOW-86D (16°55.4′S, 176°49.5′W; water depth 1990 to 1664 m), unusual barite-opal rocks were sampled. They are opal-cemented hyaloclastites containing fragments of tholeiitic basalt as glass, palagonite, plagioclase, and rare augite in addition to authigenic montmorillonite, phillipsite, and barite crystals.

There is considerable variation in the percentages of opal, hyaloclastite, and particularly barite in the total rocks (*3*). The relative abundances obtained by point counts on thin sections generally compare favorably with those obtained by other methods, except in rock K, where the discrepancy is probably due to the irregular opal distribution in layers and veins.

The euhedral barite crystals average 200 μm in length, with some crystals as large as 500 μm. The crystals are larger than those generally found in deep-sea sediments. Church (*4*) usually found barites smaller than 5 μm and only rarely in the size range 30 to 100 μm. In two rocks (A and B) barite is uniformly distributed, whereas in rock K it occurs only as a vein lining. The opal lines the intergranular cavities and cements the clasts. It has a botryoidal or colloform texture, with individual hemispheres 10 to 25 μm in diameter. This texture is well illustrated in Fig. 1, A and B. The occurrence of an opal vein cutting both a volcanic clast and the opal cement in rock K indicates at least two periods of opal deposition. In Fig. 1B the opal lines a cavity and surrounds a euhedral barite crystal. Optically, the opal is isotropic and has a refractive index varying between 1.440 and 1.444. X-ray diffraction of the opal gives a low broad peak between 19° and 26° with a maximum of 22° (values are 2θ for CuKα radiation, where θ is the Bragg angle); this classifies it as opal-A according to the scheme of Jones and Segnit (*5*). Opal-A commonly occurs in sediments from the deep sea, but only as radiolarians, diatoms, silicoflagellates, and sponge remains. Inorganic opal-A is not observed, probably because silica concentrations in pore waters rarely approach the equilibrium solubility value for amorphous opal, but possibly also because it is difficult to distinguish from organic opal. Organic opal-A, opal-CT (disordered cristobalite-tridymite), and quartz are the forms of silica found in deep-sea sediments (*6*). Opal-CT, in such sediments, characteristically ex-