The customary insolation curve at 65°N (Fig. 3A, solid line) shows an insolation maximum at around 48,000 years B.P. Failure to find evidence for a high sea-level stand corresponding to this insolation maximum compelled Broecker (*3*) to give the precession effect relatively more weight than the tilt effect, implying that the temperature-sensitive latitudes in the ice-climate system are farther south than 65°N. With this weighting the prominent insolation maximum at 48,000 years is suppressed, while at the same time a new and distinct insolation high appears at 105,000 years (Fig. 3A, dashed line). This argument is strengthened by the Barbados data (*4*) which show some evidence for a separate high sea stand at about 102,000 years B.P. We were unable to directly date such a high sea-level stand in New Guinea, although the field evidence indicates a distinct transgression between the "80,000"- and "125,000"-year sea stands which almost certainly corresponds to the "105,000"-year stand on Barbados. However, our results from New Guinea show quite clearly that the sea stood relatively high between 50,000 and 35,000 years ago. A similar high sea stand between about 60,000 and 40,000 years ago has been reported from Kikai-Jima in the Ryukyu Islands (*18*). Failure to identify this high sea stand on Barbados can be explained by the lower uplift rate of Barbados [~ 0.3 mm/year (*4*)] as compared to that of New Guinea (1 to 3 mm/year), and especially if uplift of Barbados was nonuniform rather than uniform as assumed.

The New Guinea data independently confirm, either directly or indirectly, each high sea-level stand identified on Barbados for the last 230,000 years, thus supporting the idea that these sea level stands are indeed eustatic. The 50,000- to 35,000-year transgression found on New Guinea improves the close correlation of eustatic sea level fluctuations with predicted insolation changes in the Northern Hemisphere for the last 200,000 years. This can hardly be a coincidence and strongly supports theories of glaciation which utilize insolation changes as a controlling trigger mechanism.

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14. Correction for nonradiogenic Th^{230} was required for samples ANU 116, ANU 117, and ANU 150 which contained 0.03, 0.04, and 0.02 ppm of Th^{230}, respectively. The Th^{230} : Th^{232} ratio of 1.2 in this correction was estimated in a similar manner as suggested by A. Kaufman and W. S. Broecker [*J. Geophys. Res.* **70**, 4039 (1965)], using the Th^{232} content (0.03 ppm) and known C^{14} age of sample ANU 153. This correction introduces an additional uncertainty, because the Th^{230} : Th^{232} ratio may vary and because the time of addition of these isotopes to the shell carbonate has to be assumed.
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Polywater: Methods for Identifying Polywater Columns and Evidence for Ordered Growth

Abstract. *The refractive indices of polywater columns in glass capillaries have been rapidly and accurately measured with an interference microscope. Polywater has been detected by this method in both quartz and Vycor glass capillaries. A comparison of refractive index measurements with measurements of optical anisotropy indicates that polywater initially condenses with an ordered structure.*

Considerable interest has developed recently in the preparation and properties of polywater (*1*), a form of water which has properties quite different from those normally associated with liquid water. We have applied two practical methods of measuring refractive index to the problem of identifying polywater columns in capillaries. The methods are rapid and simple and make use of an interference microscope. Earlier methods of identifying polywater have required the removal of some of the polywater from the capillary (*1, 2*), or use of an uncommon measuring apparatus (*1, 3*), or a minimum column length of 2 to 3 mm (*4*). In contrast, the methods for measuring refractive index described here will detect even small amounts of polywater and measurements can be made directly on the polywater-containing capillaries as they result from the preparation. Moreover, one can use measurements of refractive index and optical anisotropy to draw conclusions about the growth of polywater molecules in the capillary.

Deryagin *et al.* (*3*) identified columns of polywater by measuring the refractive index η; their method is based on the fact that the liquid filling the bore of the capillary forms a cylindrical lens. The refractive index is obtained by measuring the difference in focal length between the empty and liquid-filled capillary and then referring to a calibration curve determined empirically from measurements of liquids of known η. Using this method, Deryagin *et al.* measured refractive indices of polywater in the range from 1.335 to 1.5. By comparing polywater with liquids of known refractive index, Lippincott *et al.* (*1*) found that a specimen of polywater had a refractive index of 1.48. Willis *et al.* (*5*) reported that the portion of a column of poly-

water remaining when the pressure over the capillary was decreased to 10^{-2} torr had a refractive index close to that of Pyrex glass.

We used a Zeiss Jamin-Lebedeff type interference microscope with an Ehringhaus compensator to measure the refractive index of polywater columns; these columns were prepared by the method of Anisimova *et al.* (*6*) in which water vapor is condensed in freshly drawn capillaries of fused quartz and a saturated potassium sulfate solution controls the vapor pressure. Those capillaries in which condensation occurs are sealed at both ends, placed on a microscope slide, and immersed in water under a cover glass. A 4-mm objective lens and a ×12.5 eyepiece with a micrometer scale are used to measure the outside diameter (OD) and inside diameter (ID) of the capillary. The Ehringhaus compensator is used to measure the optical path difference (OPD) between the capillary at its center and the water mount. The total optical path difference is equal to the optical path of the quartz plus the optical path of the polywater contained in the capillary bore, minus the optical path of the reference beam through the water mount. The refractive index of the polywater (η_{pw}) can be calculated as follows, where 1.33 is taken as the refractive index of the water mount and 1.46 is the refractive index of the fused quartz:

$$\eta_{pw} = [OPD + 1.33\ OD - 1.46\ (OD - ID)]/ID$$

In the calculation we presume that the capillary and bore are concentric and round in cross section and therefore that the OD and ID, as measured in the plane of the microscope stage, are the same as the thickness of the capillary and bore, respectively, in the direction normal to the stage. The principal source of error in the method results from any departure from these two assumptions. Measurements made on capillaries filled with normal water and with other liquids of known refractive index indicate that, if we exclude capillaries whose geometry is eccentric, η can be measured to within ± 0.01. In Table 1 are listed typical examples of the refractive indices measured by this method for polywater columns ranging in length from 3 to 90 μm.

An auxiliary technique useful for rapid recognition of polywater with a high refractive index, even in nonround capillaries, consists of superimposing the fringe system formed by the Ehringhaus compensator onto the fringe system formed by the capillary in the interference microscope. Each fringe of the resultant fringe system then represents a locus of points in which the optical path of the compensator is equal to, but of opposite sign, to the optical path of the capillary. A fringe will appear to pass through the bore of the capillary without deviation only if its contents have a refractive index equal to that of the capillary walls. Deviations upward or downward indicate a refractive index within the bore greater or less than that of quartz. Such deviations are shown in a photomicrograph (Fig. 1) of the superimposed fringe system for capillary 1 (Table 1) and a portion of its contents. The upper column is polywater, and the lower column is normal water.

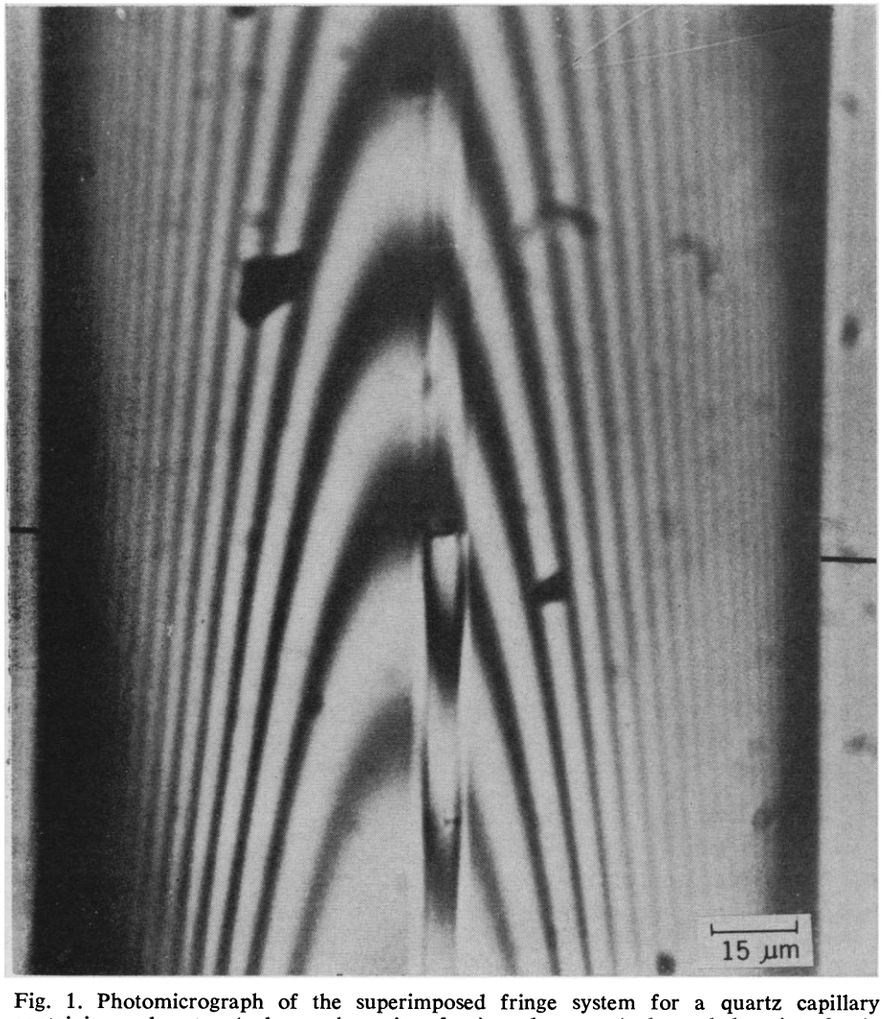

Fig. 1. Photomicrograph of the superimposed fringe system for a quartz capillary containing polywater (column above interface) and water (column below interface). The interface lies on a line between the two marks.

All of the polywater columns observed (Table 1) were in contact with water at one or both ends. The shape of the interface between the polywater and water columns (Fig. 1) appears ragged when viewed with bright field illumination. If we ignore the refractive index, the polywater specimens listed in Table 1 could be divided into two groups: (i) those whose interface with water was ragged (capillaries 1 through 4) and (ii) those whose interface was smooth (capillaries 5 through 10). Even after 2 months of storage at room temperature the respective interfaces retained their ragged or smooth character, and the refractive index of the water column remained the same (1.33).

Polywater columns were also prepared in freshly drawn capillaries of Vycor glass. The refractive index of a specimen prepared in a Vycor glass capillary (8 μm in inside diameter) was 1.39.

Substitution of a saturated solution of K_2SO_4 in D_2O (99.8 percent D, Stohler Isotope Chemicals) for the K_2SO_4 solution in the preparation pro-

Table 1. Properties of typical polywater columns in quartz capillaries at room temperature.

Capillary No.	Inside diameter (μm)	η	Δ (μm)	$f_{pw(\eta)}$	$f_{pw(\Delta)}$
1	8.00	1.51	0.3	1.0	1
2	7.17	1.46	.3	0.72	1
3	13.00	1.44	.3	.61	0.6
4	16.75	1.43	.3	.55	.5
5	11.50	1.41	.2	.44	.5
6	8.00	1.40	.2	.39	.6
7	21.75	1.38	.1	.28	.1
8	14.00	1.38	.1	.28	.2
9	14.60	1.38	.1*	.28	.2
10	64.70	1.38	.1	.28	.04

* Retardation developed after heating to 78°C.

cedure resulted in the condensation of a column of liquid in a fused quartz capillary (67.5 μm in inside diameter). The refractive index of the column was 1.38, and it is presumed that the liquid is modified D_2O since the refractive index of normal D_2O is 1.34.

The capillaries listed in Table 1 were examined between the crossed polars of a conventional polarizing microscope. The polywater columns were birefringent and showed characteristic polarization colors. Columns generally presented a domain structure of irregularly disposed regions having signs of elongation positive or negative with respect to the capillary length. The retardation Δ can be estimated from polarization colors by use of standard charts on which the value of Δ corresponding to each color is plotted (*7*). Values determined in this manner are listed in Table 1.

The polywater column in capillary 2, which originally showed a high retardation, was heated in the open capillary to 320°C. On cooling this capillary to room temperature, we observed no change in retardation or refractive index.

The values of refractive index and retardation (Table 1) were measured within a few days after preparation of the polywater columns. Remeasurement of these two properties after 2 months of storage of the capillaries at room temperature showed a striking decrease in Δ and a change of less than 1 percent in η. In those polywater columns which originally had retardations of 0.3 μm, the retardation decreased to less than 0.1 μm, whereas no retardation could be observed for those with original retardations less than 0.3 μm. Subsequent heating of the capillaries had no effect on the observed retardation. The extent of ordering of the polywater in the column, as estimated by Δ, thus decreased considerably. However, since η changes only slightly with time, we conclude that there is little change in the amount of polywater in the column.

The presence or absence of birefringence in polywater has been noted by other workers (*1*, *5*, *8*), but their polywater was either removed from the capillary or concentrated in the capillary by removal of low-boiling fractions. It is not possible in these cases, therefore, to correlate the degree of optical anisotropy with a possible growth mechanism.

The retardations tabulated in Table 1 were estimated visually and lack the numerical accuracy of the refractive index measurements. However, the consistent grouping of relatively high retardations with higher refractive indices, two properties which were determined independently of each other, merits an explanation.

The highest refractive index we have measured for as-grown columns of polywater is 1.51. The inside diameter of capillaries containing as-grown polywater of this refractive index has been 8.0 μm or less. A column of polywater of lower refractive index can be concentrated by gentle heating of the open capillary to 60°C. Removal of the more volatile components of the column results in a shorter column having an increased refractive index. After prolonged heating the column can be concentrated sufficiently to give a maximum value for the refractive index of 1.49. The concentrated column is not birefringent, and concentration to the maximum value has been carried out on capillaries as large as 18.4 μm in inside diameter.

Previously reported values for the maximum refractive index of polywater specimens are as follows: 1.48, measured on a specimen of polywater concentrated by distillation outside of the capillary (*1*); 1.5, measured on a specimen concentrated by evacuation of an unsealed capillary (*5*); 1.48 to 1.5, measured on as-grown columns of "maximally modified water" (*3*). The refractive index of 1.51 measured in capillary 1 is in the range of maximum values previously reported for polywater, and, for the purposes of explaining the grouping of high refractive index with high retardation in Table 1, we assume that this capillary contains only polywater.

The volume fraction of polywater contained in the other columns can then be estimated from refractive indices according to

$$f_{pw(\eta)} = \frac{\eta - 1.33}{1.51 - 1.33}$$

where 1.33 is the refractive index of water. These values of $f_{pw(\eta)}$ are given in Table 1.

The fraction of ordered polywater in as-grown columns can be estimated from the measured retardation values and a few simple assumptions. The retardation of an ordered structure is related to its birefringence B and its thickness t by

$$\Delta = B \times t$$

If we again assume, on the basis of its refractive index, that capillary 1 contains pure polywater, then the birefringence of ordered pure polywater is at least 0.038 (0.3/8.00). If all of the polywater contained in capillaries 2 through 10 is identical to the polywater specimen in capillary 1, then the volume fraction of polywater in these capillaries is given by

$$f_{pw(\Delta)} = \frac{\Delta}{0.038\, t}$$

where t is the inside diameter of the capillary. These values of $f_{pw(\Delta)}$ are given in Table 1.

A comparison of $f_{pw(\eta)}$ with $f_{pw(\Delta)}$ shows fair agreement. We interpret these findings, and those on the change of retardation with time, as an indication that most of the polywater in a column grows as a highly ordered layer near the capillary wall. As the distance from the wall increases in a freshly prepared column of polywater, both the amount of polywater and the extent of ordering decrease. Our observations suggest that ordered layers can be grown up to 4 μm thick (one-half the inside diameter of capillary 1) but that thinner layers are probably more common.

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Rangia cuneata on the East Coast: Thousand Mile Range Extension, or Resurgence?

Abstract. Rangia cuneata, *a valuable clam of the estuarine zone where fluctuating salinities (from 0 to 15 parts per thousand) exclude most animals, is now developing large populations in many estuaries from Florida to Maryland. Before 1955 it was thought to be extinct on the East Coast since the Pleistocene and to be living only in Gulf Coast estuaries.*

The brackish-water clam *Rangia cuneata* (Gray in Sowerby, 1831) is a member of the marine family Mactridae but is included in some freshwater handbooks (*1*). As a living species, its range was until recently always designated as Gulf Coast estauaries of the United States and Mexico (*1, 2*). The Pleistocene range is said to have been much broader, extending north as far as New Jersey (*3*). On the Atlantic Coast from Florida to New Jersey, shells of *R. cuneata* are common in many places but have always been considered very old, mostly Pleistocene. No living individuals were reported from the East Coast until a few years ago. Now the species is extremely abundant in many estuaries from Florida to northern Maryland, and is apparently still increasing.

Wells (*4*) listed *Rangia cuneata* among the species living "in the substrate between oysters or under them" in Newport River, North Carolina, in 1955–1956. This seems to be the first recorded finding of living *R. cuneata* on the Atlantic Coast. Godwin (*5*) described dense populations of this species in the Altamaha River delta, Georgia, and quoted J. P. E. Morrison as saying that specimens had been collected there "at least as early as 1958." In Virginia (*6*) living *R. cuneata* were found in 1960 by W. G. Hewatt in Back Bay near the North Carolina line, where it was abundant by 1962, and Jon Shidler found the species living in the James River in 1963. Pfitzenmeyer and Drobeck (*7*) found *R. cuneata* abundant at several places in the Potomac River, Maryland, and gave reasons for believing that it had not been there before 1960. Chanley (*8*) reared the swimming larvae from James River *Rangia*, and quoted Morrison as believing that the "scattered populations" in Maryland and Virginia had been established longer than the 5 years suggested previously (*7*). Wolfe (*9*) measured ^{137}Cs in large populations of *R. cuneata* in the Neuse River and its tributary the Trent in North Carolina. Wolfe and Petteway (*10*) measured growth of clams in the dense Trent River population. Also in North Carolina, Tenore *et al.* (*11*) studied the effect of substrate on growth of *R. cuneata* from the Pamlico River population, which they described as abundant in a 64-km stretch, from fresh water to water of 18 parts per thousand (ppt) salinity at the river mouth.

In 1969 *R. cuneata* is even more abundant and widespread on the East Coast. It now occurs in the upper end of Chesapeake Bay and in the Sassafras River in northern Maryland (*12*), probably in other Maryland rivers, and certainly in several Virginia rivers. It seems well on the way to reoccupying all the range occupied in Pleistocene or warmer Recent times. *Rangia* populations now "pave the bottom" in many places where frequent sampling revealed none a few years ago. Shellfishery biologists familiar with the phenomenon have two theories: (i) that *R. cuneata* is a recent invader from the Gulf Coast, or (ii) that some unknown ecological change sparked resurgence of a small undiscovered population surviving since the Pleistocene in East Coast rivers. Either explanation is hard to believe, but it is undeniable that we are now witnessing a population explosion.

The distribution of *Rangia* in an estuary overlaps that of *Crassostrea virginica,* but *R. cuneata* becomes much more abundant farther up the estuary where the salinity, usually 0 to 10 ppt, is too low for oysters and for almost all other estuarine competitors or influents. A population of *R. cuneata* 40 to 50 km above the mouth of the Neches River in Texas lives in fresh water (salinity below 0.3 ppt) for at least 7 months of the year, and in salinity up to 13 ppt during low river periods, without apparent mortality. This population averages approximately 250 4-year-old clams (45 mm long) per square meter. It was estimated to produce annually 12,400 pounds of shell and 2,560 pounds of meat (wet weight) per acre (13,900 kg of shell and 2,900 kg of meat per hectare). At current prices paid to producers, the shell would be worth $25 and the meat more than $750 for a total value of at least $775 per acre ($1914 per hectare) per year (*13*). *Rangia cuneata* is of enough economic value and food value to justify expenditures to keep rivers free from pollution. It is also an ecological asset because it converts detritus into meat feeding many fishes and crustaceans (*11, 14*). It is an especially desirable addition to the estuarine fauna because it populates the zone of salinity tension where few other invertebrates can live.

On the Gulf Coast *R. cuneata* tolerates water temperatures as low as 3°C for at least a few hours, and as high as 32°C for months, without conspicuous mortality. Some mortality does occur even under "normal" conditions, however, and there are occasional die-offs without apparent cause. The Maryland populations either must withstand water temperatures lower, for longer periods, than Gulf populations ever encounter, or they will be killed by severe winters. Much of the basic information needed is still lacking, and *R. cuneata* remains perhaps the most mysterious of our common mollusks (*15*).

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