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$$G_{helix} = G_{solvation} - RT \ln z_{vib} \qquad (1)$$

$$G_{coil} = G_{solvation} - RT \ln z_{vib} - RT \ln \alpha_{torsion} \qquad (2)$$

where G_{helix} and G_{coil} are the free energies of the helical and random coil parts of conformation space (*10, 26*). In each case, the solvent-accessible surface area of an energy-minimized helical or extended conformation was determined, and semi-empirical relations were used to map this area to a free energy of solvation, $G_{solvation}$ (*27*). For both G_{helix} and G_{coil}, the vibrational partition function z_{vib} was calculated with a normal mode analysis about the local minimum. In G_{coil}, $\alpha_{torsion}$ corrects z_{vib} to include full rotational torsion about the acetylene bridges, and these torsion angles were taken to be independent of one another. Both z_{vib} and $G_{solvation}$ were essentially identical for any of the extended, planar local minima chosen to represent the nonhelical ensemble.
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22. With the use of vapor pressure osmometry, the intermolecular association constants K_a of **1** to **6** could be reliably measured in acetonitrile at 37°C. K_a increases with *n*: For example, $K_a(\mathbf{2}) = 8 \pm 3\ M^{-1}$, $K_a(\mathbf{4}) = 49 \pm 14\ M^{-1}$, and $K_a(\mathbf{6}) = 1186 \pm 143\ M^{-1}$. If variation in $K_a(\mathbf{6})$ over small changes in temperature is neglected, only ~3% of **6** is expected to be involved in bimolecular aggregates at 10 μM and 25°C. In each case, K_a was determined with a model that assumes K_a is the same for the dimer and all higher-order aggregates.
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A Mound Complex in Louisiana at 5400–5000 Years Before the Present

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An 11-mound site in Louisiana predates other known mound complexes with earthen enclosures in North America by 1900 years. Radiometric, luminescence, artifactual, geomorphic, and pedogenic data date the site to over 5000 calendar years before present. Evidence suggests that the site was occupied by hunter-gatherers who seasonally exploited aquatic resources and collected plant species that later became the first domesticates in eastern North America.

Native American mounds have been recognized and studied in the eastern United States for more than a century. They represent early evidence for organized society in North America. Most of the earthen mounds and enclosures in the east date to <2500 calendar years before present (B.P.) (*1*). In the 1950s, the recognition of preceramic mounds and earthen enclosures from earlier times came first at the Poverty Point site in Louisiana, dating to 3500 calendar years B.P. (*2, 3*). By the 1970s, four mound sites in Louisiana and one in Florida had been dated to >5000 calendar years B.P. (Middle Archaic), but the data were not conclusive and the antiquity of the sites remained in doubt (*4, 5*).

In the 1990s, four additional mound sites in Louisiana (*6–8*) and two in Florida (*8*) have been identified as Middle Archaic in age. Collectively, the Middle Archaic mound sites provide 56 radiometric dates that establish the antiquity of earthen mounds in the southeast. Of these sites, Watson Brake in northeast Louisiana is the largest, most complex, and most securely dated site. Its 11 mounds and connecting ridges form an oval-shaped earthen enclosure 280 m in diameter (Fig. 1). The largest mound (Gentry Mound) is 7.5 m high; the other mounds measure between 4.5 and 1 m in height, and the connecting ridges average 1 m in height. Here we present evi-

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dence that Watson Brake predates the large-scale earthworks of Poverty Point by 1900 years, making it the earliest such human construction so far recognized in the New World.

Watson Brake is constructed on the edge of a low, flat Pleistocene terrace (Mid-Wisconsin stage) overlooking the Holocene floodplain (<12,000 calendar years B.P.) of the Ouachita River (*9*, *10*). Before 7000 calendar years B.P. (*10*), meander belts formed by the paleo–Arkansas River provided gravel and sand shoal channels in the Ouachita Valley, and swamp and small-stream habitats formed in backwater areas near Watson Brake. These conditions persisted until about 4800 calendar years B.P., when a diversion of the Arkansas River into the present course of the Ouachita River caused rapid alluviation near Watson Brake (*10*), decreasing the extent of the swamp and small-stream habitats. This event may coincide with abandonment of the site.

We verified the cultural origin of each mound and ridge with eight test units and soil cores. Mounds and ridges along the edge of the Pleistocene terrace were constructed in multiple stages and on premound or ridge middens (*11*). Mounds and ridges set back from the terrace edge were constructed in single stages and on the truncated Bt horizon of the Pleistocene terrace (the A horizon was removed before mound or ridge construction). This removal suggests that mound and ridge placement on the north and east sides followed the natural topography, whereas mounds and ridges on the west and south sides of the enclosure were placed to complete the enclosure. The extensive weathering of fill in the single- and multiple-stage mounds and ridges suggests that all of the earthen structures are contemporaneous.

The physical, chemical, and morphological properties of soils that developed in the mounds and ridges indicate that the earthen architecture is of great antiquity. These soils are strongly weathered, with well-expressed A-E-Bt horizonation (Ultisols and Alfisols). A typical profile consists of a 1-m solum with a fine sandy loam ochric epipedon (A horizon), a fine sandy loam to loamy fine sand albic (E) horizon, and a reddish, clay-enriched argillic (Bt) horizon. The Bt horizons are 40 to 80 cm thick and have fine and medium subangular-blocky structure. Clay translocation, which leads to the development of the Bt horizons, is pronounced as indicated by (i) clay depletion of the overlying A and E horizons, (ii) enrichment of the Bt horizons in clay content relative to overlying horizons and underlying unweathered mound fill, (iii) high ratios of fine clay to total clay in the Bt horizons, and (iv) the presence of argillans (clay coatings) in the Bt horizons. The argillans have variable thickness (100 to 300 μm) and are composed of microlaminated clay. Extensive leaching is indicated by low concentrations of exchangeable bases (Ca, Mg, Na, and K) and pH of 5.1 to 3.9 to great depths. Base saturation ranges from 10 to 51% in the Bt horizons. Iron has leached from the A and E horizons (0.3 to 0.5%) and illuviated into the Bt horizons (0.9 to 1.1%).

The strongly developed soils on the mounds and ridges at Watson Brake may be partially attributed to the nature of the material used to construct these features. Emplacement of weathered (preconditioned) material during the final stage of mound and ridge construction would favor rapid pedogenesis. However, the formation of thick Bt horizons that meet argillic criteria is time-dependent because weathering, clay formation, and translocation are slow processes (*12*). Hence, we suggest that the Ultisols and Alfisols developed in the mounds and ridges are products of thousands of years of pedogenesis.

We obtained 19 radiocarbon assays from buried A horizons on the premound and preridge surfaces as well as from the surfaces of successive stages of mound and ridge construction (Table 1). Two of the dates are considered anomalous because of their younger-than-expected age (*13*). Dates on four charcoal scatters from submound and subridge A horizons (mounds A, B, and C; ridge K/A) range between 5880 and 5450 calibrated (cal.) calendar years B.P. Dates for soil humates from two submound A horizons (mounds A and D) are 5285 and 5450 cal. calendar years B.P. These dates suggest that mound construction at Watson Brake began between 5400 and 5300 calendar years B.P.

Six charcoal samples from buried A horizons on successive stages of mound B and stage I of ridge K/A yielded radiocarbon ages between 5590 and 5290 cal. calendar years B.P., and humates from four buried A horizons in mounds A, C, and D range in age between 4870 and 4520 cal. calendar years B.P. In addition, humates from a pit-hearth in the surface of stage I, mound C dates to 4826 cal. calendar years B.P. On average, the humate ages are 700 years younger than the charcoal ages. The humate ages appear to be too recent because of postburial input of organic carbon. Soil organics are susceptible to contamination by modern rootlets, humic acids, and other sources of young carbon, which can yield anomalously young radiocarbon ages (*14*, *15*).

Independent means of determining the antiquity of Watson Brake include lumines-

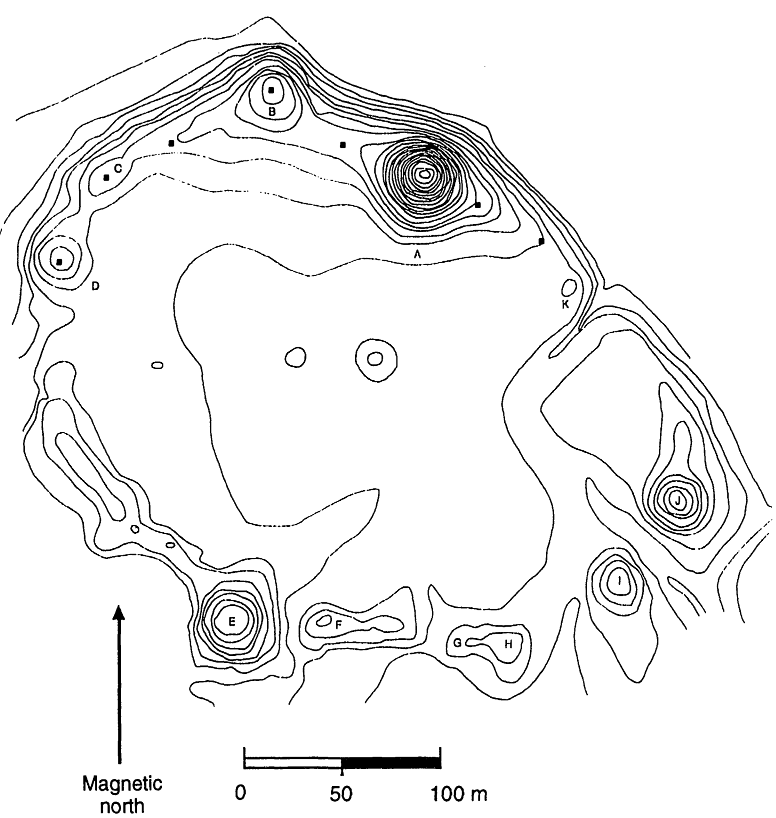

Fig. 1. Watson Brake topographic map. Black squares indicate test units. Test unit 5 is an extension of test unit 4 in mound C; thus there are only seven squares on the map. Contour interval = 0.5 m.

cence dating of mound and ridge sediments (16). We examined samples from the buried A horizons of stage I, mound B and stage I, ridge K/A. It was hypothesized that the formation of A horizons on the intermediate stages had provided adequate time for bleaching of sediments through recycling to the surface by pedoturbation. Thermoluminescence analysis of the slowly bleaching component in quartz produced geological rather than archaeological ages, which suggests that bleaching was incomplete. Optically stimulated luminescence (OSL) of the rapidly bleaching component using single aliquot analysis (17) yielded an age of 4003 ± 444 calendar years B.P. for ridge K/A and a maximum age of 5538 ± 936 calendar years B.P. for mound B. The OSL signal for the ridge sample appeared well bleached in antiquity, but variation in equivalent dose from aliquot to aliquot suggested that bleaching of the mound B sample was incomplete.

The mean residence time of three mounds and two ridge segments was calculated with the experimental dating method of oxidizable carbon ratio (OCR). The OCR procedure measures biochemical degradation of organic carbon within the site-specific environmental context (18, 19). Analysis of 200 soil samples suggests that the submound soils were buried with mound fill, thereby arresting biochemical degradation, at ~5180 ± 155 calendar years B.P. and that mound fill pedogenesis began at ~5010 ± 150 calendar years B.P.

Artifactual data support a pre–Poverty Point (>3500 years B.P.) origin for the mounds and ridges. None of the Poverty Point archetypes (20, 21) have been recovered from Watson Brake. Projectile points from Watson Brake are Middle to Late Archaic in age (22). Lithic material is local gravel, in contrast to Late Archaic and Poverty Point sites, where nonlocal material is common (23, 24). Blade production at Watson Brake is casual, with minimal platform preparation and no platform rejuvenation. At Poverty Point, blade cores have more formal platform preparation and blade removal (25). Watson Brake blades frequently were transformed into microdrills for bead production, averaging 9.9 by 2.7 by 2.2 mm. This technology is similar to the Middle Archaic assemblages from east central Louisiana (26) as well as from the Keenan Cache (27) and the Slate Site (28) in Mississippi.

Local gravel was used for cooking stones at Watson Brake. In addition, fired earthen objects (function unknown) occur in a variety of undecorated shapes (cuboidal, rectangular, spherical, and cylindrical); block forms are the most common. Similar fired earthen objects have been recovered from Frenchman's Bend Mounds, a Middle Archaic site 35 km northeast of Watson Brake (7). There, mound deposits with fired earthen blocks date to 5570 (7) and 5290 cal. calendar years B.P. (β69637, 4560 ± 140 corrected, uncalibrated ^{14}C years B.P., charcoal scatter), which is about the same age as that of Watson Brake specimens. Undecorated blocks have not been found at Poverty Point.

Over 175,000 pieces of bone were recovered from mound B, stage I and its submound surface. Aquatic species predominate and fish are the most abundant food remains. Main channel species were preferred, including freshwater drum (Sciaenidae), catfish (Ictaluridae), and suckers (Catostomidae). Additional aquatic foods include 17 mussel species (Unionidae), one aquatic snail (thousands of *Campeloma* sp.), turtle, and duck. Deer, turkey, raccoon, opossum, squirrel, rabbit, dog, and rodent remains also were recovered from the midden.

Charred seeds from the same midden deposits represent three species of the complex of weedy annuals (29). These include goosefoot (*Chenopodium berlandieri*), knotweed (*Polygonum* spp.), and possibly marshelder (*Iva annua*). The morphology of the goosefoot seeds is consistent with var. *boscianum*, a taxon uncommon in the area today. None of the seeds exhibit morphological features associated with evolution under cultivation. However, their presence may reflect the early development of ecological relationships that eventually led to domestication.

The fauna and flora suggest that Watson Brake was occupied seasonally. Fish otoliths indicate that most fish were caught in spring to early summer and fall. The spring to early summer peak probably corresponds with the spawning of the freshwater drum (*Aplodinotus grunniens*). The plant species seed in the summer through fall, also suggesting seasonal occupation of the site.

Increases in terrestrial species coupled with decreases in mussel and slackwater fish between the earlier premound midden and the later stage I midden of mound B may reflect a change in the local environment. The decline in the main channel, gravel/sand shoal habitats, backwater swamps, and small-stream habitats near Watson Brake may have resulted in a shift from aquatic resources to terrestrial species, eventually leading to site abandonment.

Geomorphic, pedogenic, radiometric, luminescence, and artifactual data have established the Middle Archaic age of Watson Brake. Faunal and floral data show that the site was constructed and occupied by hunter-gatherers who seasonally exploited riverine animals and plants. Planned large-scale earthworks such as Watson Brake were previously considered to be beyond the leadership and organizational skills of seasonally mobile hunter-gatherers. Poverty Point was considered the exception, and its extensive trade was cited as evidence for sophisticated socioeconomic organization (20). Our data imply that less complex mound building societies flourished in the southeast more than 1900 years before Poverty Point. Furthermore, not only did these Middle Archaic societies establish monumental architecture in the southeast, but they also may have initiated ecological

Table 1. ^{14}C dates from Watson Brake. Rg, ridge; Md, mound.

Provenience	Material	Lab number*	Age in radiocarbon years B.P.†	Calibration curve intercept (years B.P.)‡	Dendrocalibrated 2σ age range (years B.P.)§
Rg K/A, subridge	Charcoal scatter	β72670	5070 ± 110	5883	6000 to 5593
Rg K/A, stage I	Charcoal scatter	β72669	4840 ± 170	5591	5931 to 5242
Rg K/A, stage I	Charcoal piece	β66045	4610 ± 90	5309	5492 to 5029
Md B, submound	Charcoal scatter	β82009	4960 ± 120	5703	5941 to 5455
Md B, stage I	Charcoal scatter	β80792	4660 ± 110	5442	5606 to 5034
Md B, stage II	Charcoal scatter	β72671	4610 ± 90	5309	5492 to 5029
Md B, stage II	Charcoal scatter	β72512	4860 ± 100	5596	5761 to 5442
Md B, stage II	Charcoal scatter	β72672	4550 ± 110	5288	5468 to 4872
Md A, stage I	Humates	TX9003	4361 ± 71	4870	5081 to 4822
Md A, submound	Charcoal scatter	β95000	4690 ± 130	5450	5665 to 4987
Md A submound	Humates	TX9004	4540 ± 58	5285	5326 to 5021
Md C, stage I hearth	Organic fill	β93880	4220 ± 60	4826	4779 to 4567
Md C, stage I	Humates	TX9002	4200 ± 63	4822	4860 to 4563
Md C, submound	Charcoal scatter	β95002	4700 ± 90	5452	5613 to 5253
Md D, stage III	Humates	TX9005	4046 ± 49	4517	4645 to 4406
Md D, stage I	Humates	TX9007	4329 ± 64	4864	5054 to 4815
Md D, submound	Humates	TX9006	4702 ± 53	5452	5497 to 5307

*β, Beta Analytic; TX, Radiocarbon Laboratory, University of Texas. †Uncalibrated $^{13}C/^{12}C$-corrected ^{14}C age of specimens in ^{14}C years B.P. (±1σ). ‡Intercept between the conventional ^{14}C age and the dendrocalibrated calendar time scale, in calendar years B.P. (Radiocarbon Calibration Program 1993, rev. 3.0.3c; M. Stuiver and P. M. Reimer). §Two-sigma dendrocalibrated age range for specimens, in calendar years B.P.

relationships that led to the eventual domestication of weedy annuals in eastern North America.

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Reversible Nanocontraction and Dilatation in a Solid Induced by Polarized Light

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Reversible, controllable optical nanocontraction and dilatation in a chalcogenide glass film was induced by polarized light, and a direct correlation of this optomechanical effect with the reversible optical-induced optical anisotropy (dichroism) also exhibited by the chalcogenide glass was observed. A microscopic model of the photoinduced, reversible structural phenomenon responsible for the optomechanical behavior is presented. The ability to induce an anisotropic optomechanical effect could form the basis of a number of applications, including polarized light-dependent optical nanoactuators, optomechanical diaphragm micropumps, and even motors driven by polarized light.

So far, only piezoelectric and electrostrictive positioning devices have the potential to meet the accuracy demands in nanotechnology, which require movement and measurement with nanometer-scale precision (*1*). Here we show that certain amorphous semiconducting materials exhibit an optomechanical effect that is solely dependent on the absorption of polarized light. This effect could be exploited to make devices that would supplement or substitute the presently available range of electric field–dependent piezoelectric devices.

Reversible photoinduced anisotropy (PA) can be induced by polarized light (so-called vectoral phenomenon) in chalcogenide glasses (*2*, *3*). By using this effect, a previously optically isotropic chalcogenide glass sample can be made linearly or circularly dichroic or birefringent after the absorption of linearly or circularly polarized light, respectively. Current views on the structural origin of PA can be classified into two groups. The first group ascribes PA to a variety of relatively isolated atomic events that occur at short length scales, mainly on the basis of the spatial redistribution of covalent bonds (*2*), directional changes in the electric dipole moment arising from defect sites (*4*), or lone-pair electron orbitals (*5*) inherent in chalcogenide glasses. The second group invokes the orientation of structural elements that interact at longer length scales, that is, pseudocrystal-like structures (*6*), or the cooperative effect of local anisotropic events resulting in a global distortion of the amorphous network (*5*).

Our investigations show that upon irradiation with polarized light, thin amorphous films of $As_{50}Se_{50}$ exhibit reversible nanocontraction parallel to the direction of the electric vector of the polarized light and nanodilatation along the axis orthogonal to the electric vector of the light. This behavior can be interpreted in terms of a network-related mechanism for this reversible optomechanical and PA effect.

A direct method for the determination of stress in thin films involves the bending of a microbeam (cantilever), in which a change in the stress of a film deposited on one side will cause the film-cantilever structure to bend to minimize its stored strain energy. If, for instance, the tensile stress in the film deposited on the top surface of the cantilever increases, the film tends to contract and the cantilever bends up.

We focused a probe laser onto the end of a cantilever and measured the bending of the beam by the movement of the reflected laser spot on a position-sensitive photodiode; the deflection of the cantilever is linearly dependent on the current output. We used commercially available V-shaped atomic force microscope microcantilevers. They are fabricated from silicon nitride with typical dimensions of 200 μm in length, 20 μm in width, and 0.6 μm in thickness, and the bottom surface is coated with a thin layer of gold (~20 nm thick) that increases the optical reflectivity for the probe laser beam. A thin amorphous $As_{50}Se_{50}$ film (250 nm thick) was evaporated on to the top surface of the cantilever. As demonstrated previously (*7*, *8*), a composite cantilever is sensitive to thermal changes, for example, when heated by another laser beam incident on the top surface. This phenomenon, the bimetallic effect, results from the differential thermal expansion of the two bonded materials. The total stress change in a deposited film is therefore the sum of two components: the internal and thermal stresses. The internal stress is related to differences in the structure, which, for this experiment, was modified by a change in polarization of the light

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