

on the epoxidation mechanism. In static conditions (0.02 mmol of catalyst, 2.5 mmol of olefinic substrate and 2.5 mmol of oxidant added together to 5 ml acetone at 293 K), a conversion of 31% (43 turnovers) with an epoxide selectivity of 39% (80% *trans* and 20% *cis*) is found. The high percentage of stereoretention in this case, and the relatively low amounts of allylic oxidation, rule out radical oxidation by the Haber–Weiss mechanism as the major mechanistic pathway. In epoxidations with Mn(porphyrin) and Mn(TPP), axially coordinating nitrogen bases increase the reaction rate, the selectivity in epoxide formation and the stereoselectivity^{9,10}. A similar influence is probably exerted by the pyridyl that is *trans* to the oxygen in [cMn(bpy)]²⁺-Y. Hydrogen peroxide is activated by formation of a high-valent manganese species (for example, Mn(IV)=O) which forms a transition-state complex with the olefin. The oxene is probably inserted into the double bond of the olefin, which may or may not be coordinated itself to the Mn, thus giving different possible directional attacks. □

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SUPPLEMENTARY INFORMATION. Full details of the ESCA measurements, DRS and FTIR spectra (before and after catalytic operation) and SEM data are available on request. Requests should be addressed to Mary Sheehan at the London editorial office of *Nature*.

Extreme and persistent drought² in California and Patagonia during mediaeval time

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STUDIES from sites around the world^{1–5} have provided evidence for anomalous climate conditions persisting for several hundred years before about AD 1300. Early workers emphasized the temperature increase that marked this period in the British Isles, coining the terms 'Mediaeval Warm Epoch' and 'Little Climatic Optimum', but many sites seem to have experienced equally important hydrological changes. Here I present a study of relict tree stumps rooted in present-day lakes, marshes and streams, which suggests that California's Sierra Nevada experienced extremely severe drought conditions for more than two centuries before AD ~ 1112 and for more than 140 years before AD ~ 1350. During these periods, runoff from the Sierra was significantly lower than during any of the persistent droughts that have occurred in the region over the past 140 years. I also present similar evidence from Patagonia of drought conditions coinciding with at least the first of these dry periods in California. I suggest that the droughts may have been caused by reorientation of the mid-latitude storm tracks, owing to a general contraction of the circumpolar vortices and/or a change in the position of the vortex waves. If this reorientation was caused by mediaeval warming, future natural or anthropogenically induced warming may cause a recurrence of the extreme drought conditions.

The Sierra Nevada is a high-elevation (to 4,400 m), 600-km-long fault block which trends northwest–southeast. Frontal passage between November and May accounts for >85% of the Sierran rain- and snowfall. Precipitation increases towards the east as the range crest is approached, at which point the average annual total approaches 2,000 mm. It decreases abruptly to the lee, averaging ~250 mm along the base of the eastern front.

Runoff at middle and high elevations is very seasonal, reaching a sharp peak during the months of greatest snowmelt (typically May–July). The Sierra is California's most important catchment area, providing two-thirds of the state's developed surface-water supply to its huge urban and agricultural systems.

Until recently, the most severe and persistent drought of California's instrumental record occurred between 1928 and 1934 (the 'Dust Bowl period'), when Sierran runoff averaged ~70% of normal. That interval was matched in severity during the 6 years 1987–1992, reinforcing the notion of a maximum 6- to 7-year dry spell. Evidence of mediaeval droughts that were of greater severity, and far greater duration, than either the Dust Bowl or the modern periods, appears at four sites in and adjacent to the central Sierra: Mono Lake, Tenaya Lake, the West Walker River and Osgood Swamp (see Table 1 for locations).

Mono Lake is a large (~18,000 ha) body of saline-alkaline water that abuts, and receives inflow from, the eastern front of the central Sierra. Because it lacks an outlet the lake fluctuates in response to climatic changes. Since 1940 the City of Los Angeles has diverted the influent streams for municipal supply, forcing a 14-m drop in lake level to an elevation of 1,942 m. But for diversions, today's 'natural level' would be ~1,957 m (ref. 6).

Two generations of relict stumps (of *Pinus jefferyi*, *Populus trichocarpa*, *Chrysothamnus nauseosus* and *Artemisia tridentata*) are rooted at low elevations on Mono Lake's artificially exposed shorelands. The oldest generation ('G-1 stumps') includes eight ¹⁴C-dated individuals with basal elevations as low as 1,941.5 m (15.5 m below today's 'natural level', and slightly below the artificially depressed surface). Dates on outermost (death-year) wood from these eight are given in Table 1. When plotted with error bars (Fig. 1), the calibrated G-1 death-year dates overlap in a 96-year interval centred on AD 1112.

The second generation of Mono stumps ('G-2 stumps'), represented by five ¹⁴C-dated individuals, stands rooted on the shorelands at elevations as low as 1,946 m (11 m below the 'natural level'). Calibrated ¹⁴C dates on outermost rings from these five (Table 1), when plotted with error bars (Fig. 1), share a 46-year interval centred on AD 1350.

The G-1 and G-2 stumps provide evidence that Mono Lake fell to exceptionally low levels on two occasions during mediaeval time. The first of the lowstands, which persisted at least 50 years (the number of growth rings in the largest of the G-1

relicts), terminated around AD 1112 (the generalized death data on the G-1 stumps). The second lowstand, also at least 50 years in duration, terminated around AD 1350 (the generalized death data on the G-2 stumps). Independently dated lake-transgressive and lake-regressive sedimentary sequences from Mono Lake⁷ (see Table 1 and Fig. 1, dates 1, 4, 6 and 16) confirm that the death of the G-1 and G-2 vegetation coincided with rises following lowstands, thus implicating drowning as the cause of death.

Because the Mono basin has been hydrographically stable (with no interbasin stream shifts) throughout Holocene time, and because tectonic warping, faulting, and lake-water displacement attributable to lake-bottom volcanism have not caused appreciable changes in lake level during the late Holocene⁸, it is reasonably concluded that on two occasions during mediaeval time low Sierran runoff drove Mono Lake to exceptionally low levels.

Tenaya Lake, 22 km west of the central Sierran crest, receives runoff from 2,100 ha of glaciated highlands (to elevation 3,335 m). This 90-ha water body is dammed by a moraine that has been breached by the effluent stream, forming a stable spillway at elevation 2,484 m. Stands of lodgepole pine (*P. contorta*) encircle Tenaya Lake down to its high-water line. Growth of trees below that line is precluded by annual inundation.

Protruding from Tenaya Lake are nine large, upright to moderately tilted lodgepole pine trunks. These snags, firmly anchored and apparently rooted, stand in 8–19 m of water. ¹⁴C assays have been run on two of these trunks. Outermost wood from the oldest of the two provides a calibrated age range equivalent to AD ~1028–1159, contemporaneous with the G-1 Mono stumps (Table 1, Fig. 1). This relict stands in 13 m of water, and displays 68 annual rings at the water line (more rings undoubtedly exist at the presently-inundated tree base). Outermost wood from the younger of the two assayed trunks yields an age range of AD 1281–1386, similar to Mono's G-2 stumps (Table 1, Fig. 1). It stands in 11 m of water, and contains 141 annual rings at water line. The presence of these drowned trunks indicates that Tenaya Lake stood more than 13 m below its spillway for over 70 years before AD ~1093, and more than 11 m below it for over 141 years before AD ~1333. Because the Tenaya basin is hydrographically stable, and because there has been no geomorphic alteration of the spillway, low inflow seems the likely cause of the lowstands.

The West Walker River originates high on the east-Sierran flank. It debouches from its east-facing canyon at an elevation of 2,015 m, then turns abruptly northward and enters a deep, narrow-bottomed gorge. Dozens of Jeffrey pine stumps stand rooted on the lowest portions of the gorge floor, drowned by the stream. Radiocarbon assays on outermost wood from five of these reveal two generations of tree growth (Table 1). The

oldest, represented by an individual with ~220 annual rings, died within the interval AD 1044–1213, contemporaneous with the first of the inferred tree-killing transgressions at Mono and Tenaya lakes. The younger generation of West Walker River stumps, including individuals with as many as 140 annual rings, produces death-dates (Table 1) whose error bars (Fig. 1) exhibit a 94-year overlap centred on AD ~1339, equivalent to the G-2 dates at Mono and Tenaya lakes.

Jeffrey pine cannot survive complete basal inundation for periods exceeding several weeks during the season of active growth (A. Leiser, personal communication), which includes the period of peak runoff in the Sierra. The presence of the drowned stumps thus indicates that for periods of >200 years during mediaeval time, stream flows remained low enough to permit widespread tree establishment and growth on the narrow gorge bottom. Because the river at, and above, the stump site is hydrographically stable, and because the narrowness of the gorge floor over much of the stump-studded reach prevents horizontal stream shifts that would allow trees to colonize newly abandoned surfaces, neither stream piracy nor lateral migration can explain the presence of the stumps. As at Mono and Tenaya lakes, low Sierran runoff provides the most plausible explanation.

Osgood Swamp (elevation 1,995 m) is a small (5.6-ha) marsh that occupies a shallow, moraine-dammed depression immediately east of the Sierran crest. Inflow is limited to seepage from the surrounding ~100 ha. Mature lodgepole pines presently surround the marsh, but they are prevented from invading by perennially saturated ground.

In 1965, a rooted stump from the marsh was collected (D. P. Adam, personal communication) that exhibited 100 annual rings. Outside wood from this specimen provides a calibrated age range (Table 1) of AD 1024–1228, widely overlapping the death-year dates on the G-1 stumps at the West Walker River and at Mono and Tenaya lakes (Fig. 1). With no apparent evidence of late Holocene geomorphic or hydrographic alteration of Osgood Swamp, the >100 years of desiccation that permitted the establishment of trees is most reasonably attributed to low Sierran runoff.

Epic drought is not only the most reasonable explanation for the existence of stumps at each one of the presently aquatic sites described above, but it is the only plausible explanation for the site-to-site contemporaneity of the stumps. The two mediaeval droughts must have been more severe than the dry spell of the past 6 years. Throughout that 6-year period Osgood Swamp remained sodden, preventing colonization by trees; in each of those years the West Walker River experienced spring- and summertime flows too high and too prolonged to permit Jeffrey pines to establish or grow on its bed; Tenaya Lake overflowed for at least several weeks during the peak snowmelt period in

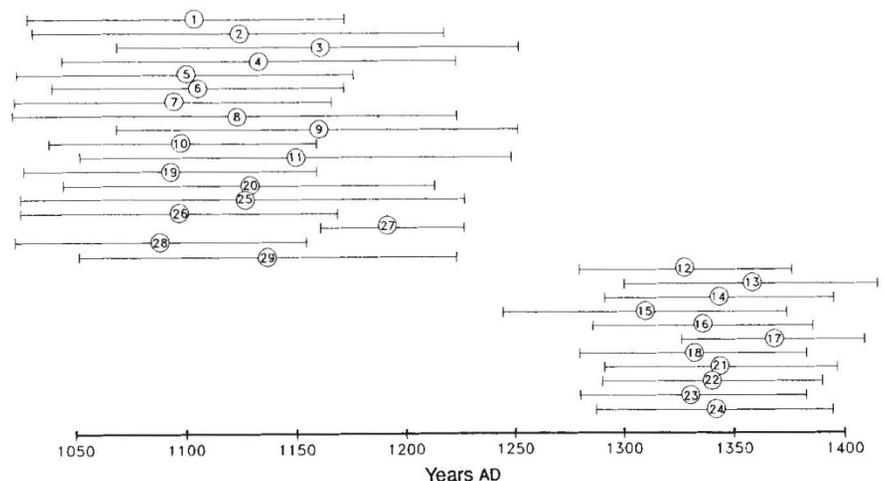


FIG. 1 Dates of drought terminations. The encircled numbers refer to the identity of the data source, as given in the first column of Table 1. The error bars represent 1σ , calculated using the program CALIB 3.0.3. (ref. 11).

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TABLE 1 Radiocarbon dates of drought terminations

Mono Lake, California (38° N, 110° W)							
ID no.	Lab.	Date (yr BP)	Calibrated date* (cal yr BP)	Sample description	Sample location	Significance	
1. USGS-1704†	Menlo	930 ± 40‡	919–782 (AD 1931–1168)	Pine cone in buried littoral sand	E. wall Rush Cr., ele. ~1,944–47 m	Dates rise from low stand of ~838 cal BP	
2. USGS-1275†	Menlo	910 ± 60	918–732 (AD 1032–1218)	Tree stump rooted on Lee Vining Cr. delta	E. of LV Cr., ele. 1,949.1 m	Dates rise from low stand of ~838 cal BP	
3. USGS-1276†	Menlo	860 ± 60	886–695 (AD 1064–1255)	Tree stump rooted on Lee Vining Cr. delta	E. of LV Cr., ele. 1,949.7 m	Dates rise from low stand of ~838 cal BP	
4. USGS-1310†	Menlo	890 ± 60	909–724 (AD 1041–1226)	Pine cone in organic-rich lake-transgr. seds	E. wall LV Cr., ele. 1,949.1 m	Dates rise from low stand of ~838 cal BP	
5. USGS-1319†	Menlo	940 ± 60	928–773 (AD 1022–1177)	Shrub stump rooted on Mono shorelands	~600 m w. of LV Cr., ele. 1,942.1 m	Dates rise from low stand of ~838 cal BP	
6. USGS-1321†	Menlo	920 ± 35	912–780 (AD 1038–1170)	Grass rooted in buried littoral sands	E. wall Rush Cr., ele. 1,944.5 m	Dates rise from low stand of ~838 cal BP	
7. USGS-1487†	Menlo	950 ± 50	928–785 (AD 1022–1165)	Tree stump rooted in Lee Vining Cr.	E. side of LV Cr., ele. 1,951.2 m	Dates rise from low stand of ~838 cal BP	
8. UCLA-118†	UCLA	920 ± 90§	931–724 (AD 1019–1226)	Tree stump rooted on Lee Vining Cr. delta	E. of LV Cr., ele. 'about 1,950 m'	Dates rise from low stand of ~838 cal BP	
9. LDGO-1677 FW†	Lamont	860 ± 60	886–695 (AD 1064–1225)	Tree stump rooted on Post Office Cr. delta	W. of PO Cr., ele. 1,947.6 m	Dates rise from low stand of ~838 cal BP	
10. LDGO-1677 LW†	Lamont	940 ± 20	914–790 (AD 1036–1160)	Shrub stump rooted on Lee Vining Cr. delta	E. wall of LV Cr., ele. ~1,947.3 m	Dates rise from low stand of ~838 cal BP	
11. CAMS-2506	Liverm	870 ± 60	898–702 (AD 1052–1248)	Shrub stump rooted on 'Little Tahiti'	Negit Islets, ML, ele. ~1,946 m	Dates rise from low stand of ~838 cal BP	
12. USGS-1277†	Menlo	700 ± 60	671–571 (AD 1279–1379)	Tree stump rooted on Lee Vining Cr. delta	E. of LV Cr., ele. ~1,951.2 m	Dates rise from low stand of ~600 cal BP	
13. USGS-1315†	Menlo	600 ± 70	650–534 (AD 1300–1416)	Non-rooted pine stmp	~300 m w. of LV Cr., ele. ~1,942.4 m	Dates rise from low stand of ~600 cal BP	
14. USGS-1167†	Menlo	640 ± 60	658–550 (AD 1292–1400)	Tree stump rooted on Lee Vining Cr. delta	E. of LV Cr., ele. ~1,947.0 m	Dates rise from low stand of ~600 cal BP	
15. CAMS-2505	Liverm	730 ± 80	710–577 (AD 1240–1373)	Shrub stump rooted on "Little Norway"	Negit Islets, ML, ele. ~1,946 m	Dates rise from low stand of ~600 cal BP	
16. USGS-1316†	Menlo	675 ± 50	663–561 (AD 1287–1389)	Pine cones in buried littoral sands	E. wall of LV Cr., ele. ~1,947.9 m	Dates rise from low stand of ~600 cal BP	
17. LDGO-1677 IW†	Lamont	570 ± 30	623–539 (AD 1327–1411)	Tree stump rooted on Lee Vining Cr. delta	~300 m e of LV Cr., ele. 1,950 m	Dates rise from low stand of ~600 cal BP	
Tenaya Lake, California (37° 50' N, 119° 27' W)							
18. Beta-46709	BetaAn	690 ± 60	669–564 (AD 1281–1386)	Tree trunk rooted in Tenaya Lake	Tenaya Lake, in 11 m of water	Dates rise from low stand of ~600 cal BP	
19. LDGO-1719 A	Lamont	950 ± 30	922–791 (AD 1028–1159)	Tree trunk rooted in Tenaya Lake	Tenaya Lake, in 13 m of water	Dates rise from low stand of ~838 cal BP	
West Walker River, California (Upstream of 'Chris Flat'; 38° 23' N, 119° 27' W)							
20. LDGO-1747 W	Lamont	904 ± 40	906–737 (AD 1044–1213)	Tree stump rooted in W. Walker River	W. Walker River near Chris Flat	Dates rewatering of WWR, ~838 cal BP	
21. Beta-46675	BetaAn	640 ± 60	658–550 (AD 1292–1400)	Tree stump rooted in W. Walker River	W. Walker River near Chris Flat	Dates rewatering of WWR, ~600 cal BP	
22. Beta-46676	BetaAn	660 ± 50	660–557 (AD 1290–1393)	Tree stump rooted in W. Walker River	W. Walker River near Chris Flat	Dates rewatering of WWR, ~600 cal BP	
23. Beta-46681	BetaAn	690 ± 60	669–564 (AD 1281–1386)	Tree stump rooted in W. Walker River	W. Walker River near Chris Flat	Dates rewatering of WWR, ~600 cal BP	
24. CAMS-2510	Liverm	660 ± 70	664–552 (AD 1286–1398)	Tree stump rooted in W. Walker River	W. Walker River near Chris Flat	Dates rewatering of WWR, ~600 cal BP	
Osgood Swamp, California (38° 51' N, 120° 28' W)							
25. I-6843		910 ± 85	926–722 (AD 1024–1228)	Tree stump rooted in Osgood Swamp	Osgood Swamp	Dates rehydration of OS, ~838 cal BP	
Argentine Patagonia (Lago Cardiel, 48° 57' S, 71° 26' W; Catalon Marsh, 50° 28' S, 72° 58' W)							
26. LDGO-1714 N	Lamont	945 ± 50	926–783 (AD 1024–1167)	Organic detritus in lake-transgr. seds.	Rio Cardiel delta, Lago Cardiel	Dates rise from low stand of ~838 cal BP	
27. LDGO-1714 H	Lamont	864 ± 40	787–722 (AD 1163–1228)	Shrub stump rooted in buried soil	Rio Tunas delta, Lago Cardiel	Dates rise from low stand of ~838 cal BP	
28. LDGO-1714 I	Lamont	972 ± 30	929–797 (AD 1021–1153)	Organic detritus in lake-transgr. seds.	Rio Tunas delta, Lago Cardiel	Dates rise from low stand of ~838 cal BP	
29. LDGO-1747 A	Lamont	880 ± 50	899–724 (AD 1051–1226)	Tree stump rooted in marsh	Catalon marsh Lago Argentino	Dates rehydrn. of marsh ~838 cal BP	

*Calculated at 1σ using CALIB 3.0.3. (ref. 3). Work is currently underway to establish dendrochronologically the precise timing of vegetation establishment and death. Abbreviations: PO, Post Office; ML, Mono Lake; Cr., creek; E., east; W., west; ele., elevation.

† Published previously, with less precise calibration, in ref. 3.

‡ Collected by M. Perkins in 1982 (personal communication).

§ Collected by D. B. Lawrence in 1960 (ref. 12).

|| Published previously, with less precise calibration, in ref. 5.

each of the six drought years, and at no time during those years did it fall more than 1 m below its sill. Because these three drainage basins are dominated by exposed bedrock, and contain little groundwater storage capacity, just a single dry year, rather than a sequence of dry years, is needed to cause low runoff. It is not just a lack of duration, therefore, but rather a lack of both severity and duration, that makes the modern dry spell an inappropriate analog for mediaeval drought.

Ring counts on the longest-lived of the G-1 and G-2 stumps indicate that the first of California's mediaeval droughts lasted for more than 220 years before the generalized termination date of AD 1112 (thus, from before AD ~892 to around AD 1112), whereas the second persisted for at least 141 years before AD 1350 (thus, from before AD 1209 to around AD 1350). The period of increased wetness that separated the two droughts persisted for less than 100 years (from AD ~1112 to some time before AD 1209). These decades were, even by historical standards, very wet, forcing Mono Lake to rise to 1961 m—a level higher than any attained in the past 150 years, and the second-highest lake stand of the last two millennia⁷. The mediaeval period in California was thus marked not only by severe and prolonged drought, but by abrupt and extreme hydroclimatic shifts—from inordinate dryness, to inordinate wetness, and back to dryness.

Similar evidence of wetland desiccation has recently been discovered in southernmost Patagonia (locations, Table 1), in the austral belt of westerly winds. Rooted in presently existing marshes and ponds near Bahia Catalon on Lago Argentino are stumps of southern beech (*Nothofagus sp.*) that display between 50 and 100 growth rings. Radiocarbon dating (Table 1) places the date of tree death in the range AD 1051–1226. Lake Cardiel, 200 km farther north, recovered from one of its lowest stands of the Holocene at this same time, drowning shrubs rooted at low elevations on its shorelands. Outermost wood from three of the drowned stumps produce death-dates (Table 1) that fall within the interval AD ~1021–1228⁹. All four of these death dates from Patagonian vegetation lie remarkably close to the drought-termination dates derived from California's G-1 stumps (Fig. 1).

The findings presented here support the notion that the mediaeval climatic anomaly was a global phenomenon. They indicate that during much of mediaeval time the planetary ocean-atmosphere system operated in a mode unlike that of modern time. The mid-latitude storm track of the northern hemisphere probably remained to the north of California during the mediaeval droughts, either because of a contraction of the circumpolar vortex (as occurred, to a moderate degree, during the drought of 1928–1934), or because of a persistent ridge of high pressure that steered cyclonic disturbances to relatively high latitudes (as occurred during the shorter drought of 1976–1977) (J. Monteverdi, personal communication). The former condition is consistent with the position of the westerlies across mid-North America during the centuries before AD 1150, as reconstructed by Baerrels and Bryson². Vortex contraction could also account for the south Patagonian drought, though for different reasons. Because the Patagonian sites are at a higher latitude than those in California (48°–50° S, as opposed to 38°–39° N), and because they are not only leeward of, but also hydrographically isolated from, the Andes, a vortex contraction could place the zone of strongest westerly flow directly over the region, intensifying the Andean rain-shadow, and causing the inferred desiccation.

The aberrant atmospheric circulation of mediaeval time seems to have brought to some regions of the world a far greater departure in precipitation than in temperature. With this in mind, and to avoid prejudicing future palaeoclimatic analyses, reference to a 'Mediaeval Warm Period' or a 'Little Optimum', except when applied locally, should be replaced with some other phrase (for example, 'Neo-Atlantic'¹⁰ or 'Mediaeval Climatic Anomaly') that avoids a precise characterization of conditions.

California's mediaeval precipitation regime, if it recurred with today's burgeoning human population, would be highly disrupt-

tive environmentally and economically. This emphasizes the importance of considering changes in precipitation, rather than simply in temperature, when weighing the potential impacts of future global climate change. □

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Rapid cycling of high-molecular-weight dissolved organic matter in the ocean

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DISSOLVED organic matter (DOM) in the ocean is one of the largest active reservoirs of organic carbon on Earth. It is important to understand the processes by which DOM is recycled, particularly as changes in the oceanic DOM pool could affect atmospheric carbon dioxide concentrations on timescales of 1,000 to 10,000 years (ref. 1). It is commonly believed that low-molecular-weight material, which comprises 65–80% of DOM^{2–5}, is rapidly remineralized, and that high-molecular-weight material is refractory. But the average age of DOM in the deep ocean is about 6,000 years (ref. 6) which implies that a large proportion of the DOM cycles only very slowly. Here we present a study of the relative bioavailability of low- and high-molecular weight DOM in water samples taken from the northern Gulf of Mexico during a diatom bloom. Bacterial growth and respiration in the presence of high-molecular-weight DOM were respectively three and six times greater than for low-molecular-weight material. Although both of these pools undoubtedly contain mixtures of compounds with varying reactivities and turnover times, our results demonstrate that the bulk of oceanic DOM comprises small molecules that cycle slowly and are relatively unavailable to microorganisms.

The bioreactivity of oceanic DOM was investigated in May 1992 during a cruise in the northern Gulf of Mexico. Surface water was collected on the Louisiana shelf (18° 54.9' N, 89° 55.5' W) during a diatom bloom. The water sample was filtered through a 0.1-µm-pore filter to remove particulate material, and the DOM in the filtrate was separated into high-molecular-weight (HMW) and low-molecular-weight (LMW) fractions by tangential-flow ultrafiltration (~1 nm pore size, corresponding to M_r ~1,000)². The HMW fraction included all colloidal particles of size <0.1 µm. The initial concentration of dissolved organic carbon (DOC) was 152 µM, and ~30% of the DOC was HMW. A natural bacterial assemblage from the same water was added to the HMW and LMW fractions to