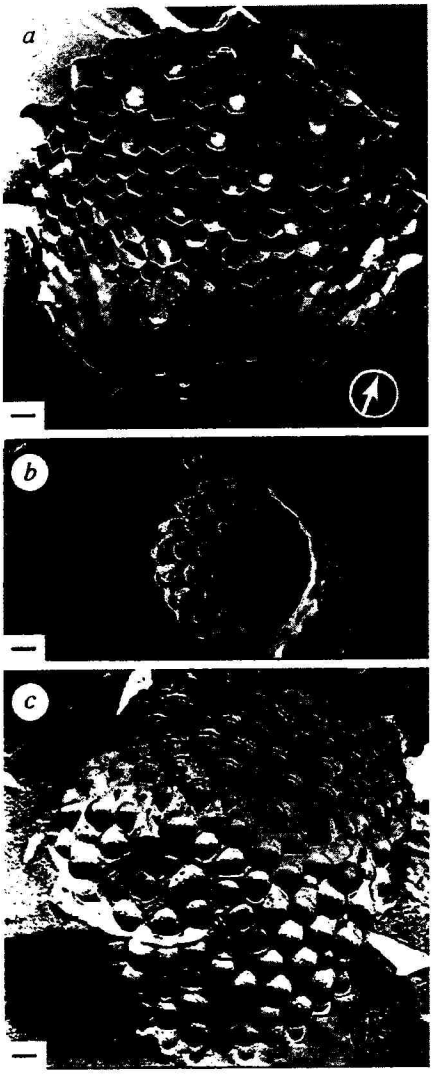
Geodesic surfactant structures

SIR — Structures formed by the self-association of amphiphiles (liquid crystals, vesicles and micelles) excite interest because of their potential uses as vectors for drug and gene delivery (see, for example, ref. 1), and as matrices from which new structured materials can be made (for example, ref. 2). We have used spherical nonionic surfactant vesicles (niosomes)[3], which are synthetic analogues of liposomes, as vehicles for drug delivery[4,5], and have identified in some of them mixtures of nonionic surfactants with cholesterol and either cholesteryl(24)polyoxyethylene ether or dicetyl phosphate. These structures include large (10–50 μm) disk-shaped vesicles, or discomes[6]. In studies on a range of niosome dispersions, freeze-fracture electron micrographs reveal related novel vesicle aggregates, which look like geodesic spheres or raspberries, respectively, and which we term 'multiniosomes' (see figure).



Freeze-fracture electron micrographs (bars represent 100 nm; shadow direction marked by circled arrow). *a*, A geodesic multiniosome. *b*, An intermediate state; the spherical shape is less clear, with no radial foreshortening (except perhaps at the left edge). Facets are convex and their boundaries are mostly unclear, except for one vertical etched line near the middle. *c*, A raspberry structure found in dispersions of sorbitan mono-oleate (Span 80). In the geodesic multiniosome, the vesicles are tightly packed and in the raspberry structure they are more loosely arranged, held together by an envelope of one or several membranes (*c*). In the intermediate state (*b*) the pressure leads to a higher degree of order in the raspberry structure (left side) and shows some features of the geodesic multiniosome form (right side).

Niosomes were prepared from sorbitan mono-oleate (Span 80), cholesterol and dicetyl phosphate (in the molar ratio 19:19:2) by dissolving the lipids in chloroform, removing the organic solvent and drying the lipid film with oxygen-free nitrogen. The dried lipid film was hydrated with distilled water and the resultant multilamellar vesicles left to cool to room temperature. The system was quenched rapidly using the sandwich technique, and metal-shadowed at –120 °C in a Balzers BAF 400D freeze-fracture system.

Examination of the cleaned replicas in a Jeol 100B electron microscope[7] revealed previously unreported structures (see figure). The most striking of these (*a* in the figure) is clearly spherical, and its surface is covered with facets, mostly flat, whose straight boundaries are deeply etched. These resemble the framework of a geodesic dome, suggesting that they are formed from a monolayer of close-packed niosomes on the surface of a large (2 μm) spherical vesicle, similar to the 'wafer structure' seen in the membranes of *Streptomyces hygroscopicus*[8], and thought to result from the hexagonal or cubic organization of membrane phospholipids between the lamellae of artificial lipid membranes.

The 'raspberry' structure (*c* in the figure) is apparently not spherical, perhaps a result of internal packing of the small spherical vesicles, either through hexagonal close-packing or in a face-centred cubic lattice. Near and parallel to the right-hand edge is a row of three squares, each with full-size spheres at the corners and smaller spheres in the centres. The smaller spheres could be the tips of vesicles from the layer beneath, positioned according to a face-centred cubic lattice. The hexagonal packing of full-size spheres over most of the bottom could represent the (111) face of a face-centred cubic lattice.

The best explanation for the raspberry structures thus seems to be that they are an aggregate of small spheres (niosomes) packed in a somewhat disordered face-centred cubic lattice. It would be simplest if the three structures in the figure were fundamentally similar, that is, that they were all niosomes close-packed to give an aggregate like a solid foam (with the gas replaced by water). The flocculation of small vesicles, either together or with a much larger vesicle, is perhaps caused by something akin to a phase separation at low temperature. Nonionic vesicles containing dicetyl phosphate have a surface negative charge, and the sorbitan head groups will have a low degree of hydration which would otherwise provide some degree of enthalpic repulsion on close approach of the vesicles at room temperature. A better understanding of such vesicle–vesicle interactions may shed light on cell–cell interactions.

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HOT and the North Pacific gyre

SIR — Karl *et al.*[1] report changes in conditions at the Hawaiian Ocean Time Series (HOT) station ALOHA (22°45′ N; 158° W) and that these indicate a significant change in the structure and productivity of the pelagic ecosystem of the subtropical North Pacific. The changes were associated with and perhaps due to an intensified near-surface stratification and a shallower mixed layer. This station is, however, unlikely to be "representative of the oligotrophic North Pacific Ocean habitat", as stated by Karl *et al.*

Station ALOHA was established to "assess and interpret annual- to decadal-scale ecosystem variability in the North Pacific subtropical gyre"[1]. Measurements there "are designed to obtain oceanographic data on the physics, chemistry and biology of this representative North Pacif-

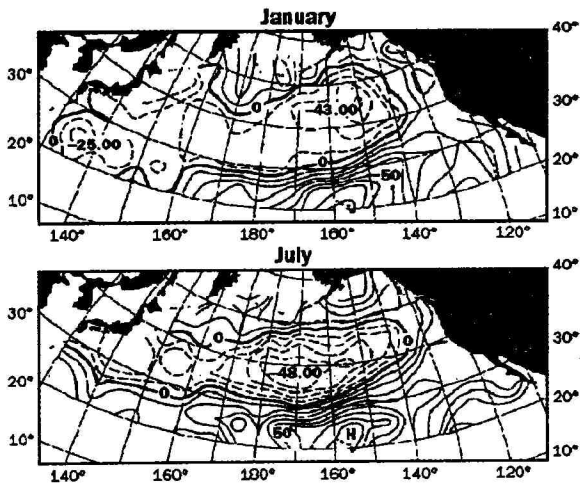
ic habitat." But Karl *et al.* cite no evidence that station ALOHA is "representative" of the oligotrophic North Pacific subtropical gyre, and there is strong evidence against this notion.

For more than 20 years, persistent, large-scale, coherent sea-surface temperature anomaly patterns have been reported in the North Pacific[2]. These are associated with long-lasting atmospheric anomaly patterns. Large sectors of positive anomaly exist concurrently with other large sectors of negative anomaly. Most of the central anticyclonic gyre is out of phase with eastern boundary currents and the ocean south of about 20° N (ref. 3). The HOT ALOHA station lies in the steep gradient between these two regimes (see figure). Monthly sea-surface temperature anomalies averaged over the 5°×5° surrounding station ALOHA are not correlated, either positively or negatively, with 5°×5° temperature anomalies over most of the central, oligotrophic gyre. These large-scale temperature anomalies at the sea surface are known to extend to at least the upper pycnocline and are accompanied by changes in upper water column physical and biological structure[4–7].

If ecosystem properties such as productivity, nutrient cycling and biomass vary in response to climatic and water column changes of the magnitude indexed by the sea-surface temperature anomaly patterns, then it is evident that studies at station ALOHA are not representative of the anticyclonic central gyre.

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KARL REPLIES — The ocean is variable on nearly all time and space scales that have been examined to date[8]. Consequently, the design of oceanographic field studies must accommodate this anticipated variability to avoid introducing a sampling or data interpretation bias. Ideally, a sufficient number of 'representative' stations in a given habitat must be revisited frequently over at least a decade, or longer. Unfortunately, this ideal sampling strategy is not practical, so intelligent compromises must be made. One approach is to establish time-series sampling stations at strategic sites that are characteristic of key oceanic habitats. This strategy was adopted by the US Joint Global Ocean Flux Study (JGOFS) programme and led to the establishment of oligotrophic ocean benchmarks near Bermuda[9] and Hawaii[10].



Contours of seasonal cross-correlations of sea-surface temperature anomaly of the 5°×5° surrounding the HOT ALOHA station (22°45′ N; 158° W) with all other 5°×5° anomalies in the North Pacific during 1947–94. Solid lines are positive, broken lines negative. H indicates the 5°×5° that includes station ALOHA (data provided by D. R. Cayan).

To date, this combined JGOFS time-series research effort of >150 research cruises on approximately monthly intervals has provided an unprecedented view of the complexity of physical and biogeochemical processes in these distinct subtropical habitats. Of general importance are the discoveries of relatively high annual rates of primary production (around 14 mols C m^{-2} yr^{-1}), the importance of N_2 fixation as a source of 'new' nitrogen and the temporal decoupling of organic matter production, export and decomposition. A hallmark of these oligotrophic habitats is variability, a remarkable departure from the previous view of a 'monotonous self-regulating climax ecosystem'[5] based on research conducted near 28° N, 155° W. Of the 18 cruises during 1971–85 (ref. 11), approximately 70% were in summer (June–September) and 5% in August alone. No cruises were conducted in 1970, 1975, 1978–79, 1981 or 1984, further time-biasing this data set.

Station ALOHA, the HOT programme site, is located at 22° 45′ N, 158° W in deep water (4,750 m), one Rossby radius (50 km) upwind of steep topography associated with the Hawaiian Ridge, but close enough to Honolulu to provide feasible logistical support. Based on an analysis of sea-surface temperature anomaly patterns over the North Pacific Ocean, McGowan disputes that our results from station ALOHA are truly representative of the anticyclonic central gyre. While this opinion may be valid, without the presentation of an equivalent, synoptic oceanographic data set on biological rates and processes from a 'representative' station, it cannot be proved definitively.

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Evolution of deuterium on Venus

SIR — Venus has a large deuterium-to-hydrogen (D/H) ratio, almost 160 times that of Earth[1]. Current models assume that Venus initially had an Earth-like D/H ratio which has risen due to atmospheric evolution. Two models have been advanced: the primordial-ocean model, which interprets the high D/H ratio as the result of the fractionation loss from a large initial reservoir of water (perhaps even an 'ocean'), and the steady-state model, where the ratio results from a balance between sources of water (probably volcanic) and fractionation losses, with the total abundance of water remaining constant over time[2]. The primordial-ocean model allows extrapolation back to the initial water abundance, whereas the steady-state model implies that this information has been lost.

Grinspoon[2,3] has argued that the steady-state model provides a good description of the current water budget, as the timescale for D/H evolution is more favourable to a steady-state solution. The steady-state model predicts a limiting D/H ratio of α/f, where α is the source D/H ratio (from, for example, outgassing) and f is the fractionation factor (describing the efficiency of D relative to H escape; f is currently 0.13; ref. 4). This creates a paradox of sorts, if the source D/H ratio is terrestrial-like, then the Venus D/H ratio should be only a factor of eight times that on Earth.

Grinspoon has proposed two solutions: either the source D/H is high, enriched by

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