particular to colloidal crystals. Our linear stability analysis of their equations¹⁹ indicates a dendritic instability at $\sim 13r_c$ (the critical nucleus $r_c \approx 3 \mu\text{m}$ for our system at $\phi = 0.504$) similar to the instability at $\sim 7r_c$ in molecular systems²⁰.

As a crystallite grows, its mass increases and in gravity it sinks faster. The viscous stresses applied to the crystallite (radius R) surfaces support its buoyant mass, M , and induce internal stresses of the order of $Mg/4\pi R^2$. When these stresses exceed the yield stress of the crystal, the crystal breaks. For a crystalline solid the yield stress, σ_{crit} is given approximately by βG , where G is the shear modulus and typically $\beta = 10^{-1}$ to 10^{-3} . Taking $M = (4\pi/3) R^3 \Delta\phi\rho$, $G \approx \chi kT/a_0^3$, $\Delta\phi = \phi_{\text{freeze}} - \phi_{\text{melt}} \approx 0.05$ and $a_0 = 0.25 \mu\text{m}$ we have $R_{\text{crit}} \approx 3\chi\beta kT/(a_0^3 \Delta\phi\rho) \approx 20h$, where h is the gravitational length ($\sim 30 \mu\text{m}$ for our samples) $\chi \approx 6$ (ref. 21), and ρ is the buoyant density of the particles. A sinking spherical particle can only grow to $\sim 600 \mu\text{m}$. Dendritic arms are sheared off much more readily. Sedimentation also sets up a flow field which can alter the diffusion field. For our samples, convection from sedimenting crystallites of radius R is faster than diffusion over the distance R when $R \geq$ several times a_0 , which may alter the growth mechanism.

The 'glass' sample that we studied had $2a_0 = 508\text{nm}$, $\phi = 0.619$, well into the glassy region observed in other ground-based systems^{22,23}. After mix-melting in normal gravity, the sample was allowed to sit undisturbed for a period of more than a year and never crystallized. The sample was mix-melted in microgravity and to our surprise began nucleation within 3.6 days. By the last experimental day of the shuttle flight the astronauts remarked on the centimetre sized crystals that had formed and filled the cell. This sample survived re-entry and sat in its fully crystalline state in our laboratory for 6 months. We then used the stirring bar in the sample cell to mix-melt the bottom half of the sample. For a month the crystalline region slowly grew into the disordered region and then essentially stopped. Figure 4 shows this sample two months after the bottom half was mix-melted. The glass region not in contact with the crystal has shown no evidence of nucleation. We therefore conclude that, at $\phi > 0.58$, the nucleation and growth of the crystals²⁴ are greatly hindered in a gravitational field. This may result from the geometry of random packings realized with and without applied stresses (for example, random close packing is $\phi = 0.64$, random loose packing, for systems under shear or gravity, is less well defined but is found to be $\phi \sim 0.58$; ref. 25).

We note that neither dendritic growth nor growth under sedimentation represent the slow quasi-equilibrium process that would assure an equilibrium crystal structure. The r.h.c.p. structure may be the equilibrium structure, but it may also result from non-equilibrium growth. The fact that f.c.c. packing was not found in microgravity but on crystalline samples brought back to normal gravity, or grown in normal gravity, suggests that stress may convert r.h.c.p. to f.c.c. One way to avoid these problems would be to use a temperature gradient to control the liquid-crystal interface (by an osmotic pressure gradient) and to 'zone refine' the samples in a microgravity environment. □

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Dissolved metals in surface sediment and a microbial mat at 100- μm resolution

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Sensors such as electrodes and optical fibre devices, optrodes, can be used to determine steep concentration gradients of chemical species in aquatic microenvironments, such as in the pore waters of surface sediments¹ and microbial mats^{2–4}, but are limited to a restricted range of determinands. The highest-resolution measurements of trace-metal concentrations in pore waters, at about 1.25 mm, have been provided by a recently developed thin-film gel technique^{5,6}, but the resultant metal distributions suggest that sub-millimetre-scale gradients need to be determined if the fluxes and cycling of the metals are to be fully quantified and understood. Here we report the development of this thin-film gel technique to measure Zn, Mn, Fe and As fluxes and concentrations at a resolution of 100 μm , and demonstrate the utility of the method *in situ* within the surface sediments and overlying microbial mat of a stream. Vertical profiles through the mat and sediments, and horizontal two-dimensional mapping just below the sediment–water interface, reveal the contrasting gradients, fluxes and remobilization niches of the four metal species at a sub-millimetre scale. The microbial mat appears to be an important regulator of the cycling of these metals. This technique has the potential to be extended to other chemical species and applied to other microenvironments with steep concentration gradients, such as redox boundaries, plant roots, animal burrows and sites of precipitation/dissolution in soils and sediments.

Microbial mats are laterally compressed ecosystems that support

most of the major biogeochemical cycles within a vertical dimension of only a few millimetres (ref. 7). The use of microsensors such as electrodes and optrodes has shown that there are steep concentration gradients (millimetres or less) of O_2 , $S(-II)$ and nitrogen species within microbial mats, reflecting the stratification of their communities^{2–4}. Although microbial mats are known to accumulate metals⁸, there have been no measurements of trace-metal concentrations within their pore waters.

In this study, we have used the technique of diffusive gradients in thin films (DGT). A layer of polyacrylamide hydrogel impregnated with Chelex chelating resin is overlain by first, a layer of hydrogel of known thickness (0.2–1 mm) and second, a cellulose nitrate membrane filter⁹. A plastic assembly ensures that only the filter contacts the solution. Metal ions freely diffuse through the 0.45- μm filter pores and the hydrogel (95% water); they are then bound by the chelating resin. After deployment the resin gel layer can be sliced, eluted with acid and metals determined by atomic absorption spectroscopy (AAS) or inductively coupled plasma mass spectrometry (ICP-MS). Deployment for a given time at a known temperature allows calculation of a simple arithmetic mean flux during deployment. In practice, apart from the first minute of deployment, this flux is unlikely to vary. If pore waters are effectively buffered by rapid resupply from a local source, such as a desorbing

solid phase, the measured flux can be quantitatively interpreted as a concentration.

With previous DGT assemblies spatial resolution was limited to 1 mm by the relatively large size of the resin beads, the difficulty of slicing a rubbery gel at submillimetre intervals, and the large size (total thickness 3–5 mm) of the assembly. We have overcome these difficulties by using a 200- μm -thick resin layer impregnated with 5% SPR-IDA (suspended particulate reagent-Iminodiacetate) chelating resin (Cetac Technologies Inc., Omaha, USA) with a 0.2- μm bead size. A 200- μm -thick layer of hydrogel is then sandwiched between the resin-gel layer and filter, and held between two 250- μm -thick Al_2O_3 ceramic plates, one of which has a 1×7.5 cm window open to the solution. The whole micro-DGT assembly resembles that of the prototype¹⁰, but has a total thickness of only 1 mm. After deployment, the resin gel is dried down using a conventional gel drier onto a cellulose nitrate filter. The filter becomes impregnated with the resin beads while maintaining the dimensional integrity of the deployed assembly. The masses of metal per unit area of the filter incorporating the dried gel were measured using proton induced X-ray emissions (PIXE)¹¹, using a similar procedure to the measurement of Fe and Mn in dried gels from diffusional equilibration in thin films (DET)¹². For measurements of vertical profiles, the 1- μm PIXE beam was rastered in

Figure 1 Concentrations of Zn, Mn, Fe and As, and fluxes of these elements to the DGT assembly, measured near the sediment surface in Sankey Brook on 5 June 1996 when the sediment was overlain by a microbial mat (5–6 mm thick). The position of the sediment surface (± 1 mm) is indicated by a broken line (at depth 0). Measurements were made by inserting a micro-DGT assembly vertically in the sediment. PIXE was used to measure the mass per unit area of metal in 100 (vertical) $\times$ 500 (horizontal) μm rasters. The PIXE calibration was confirmed to within 10% using DGT assemblies exposed to known concentrations of metals. The flux from the pore waters to the DGT assembly was measured directly. Pore-water concentrations are calculated assuming that they are well buffered *in situ*.

Figure 2 Two-dimensional representation of porewater relative concentrations of Zn, Mn, Fe and As in a plane perpendicular to the sediment surface at a position corresponding to the sediment–water interface. Concentration increases sequentially with the colour scale shown from white to yellow. The images were obtained by rastering a 1- μm proton beam (2 MeV) for 30 min in a 2.5 mm square on a micro-DGT assembly. The DGT assembly was deployed vertically in the surface sediment for 24 h.

100 × 500 μm rectangles adjacent to one another and average counts used for the rectangles. Two-dimensional image intensity maps of porewater concentrations were obtained by rastering the beam in 2.5-mm squares.

The micro-DGT assembly was deployed for 24 hours in a small polluted stream (Sankey Brook, Lancashire, UK; latitude 2° 30' W, longitude 53° 25' N). The sediment was overlain by a microbial community of *Oscillatoria*, presumably encouraged by shallow water (~60 cm), fairly stagnant conditions and a good nutrient supply. The location of the sediment–water interface and of the surface of the mat was assessed to within 1 mm, by the adherence of particles on the retrieved assembly. The resulting trace-metal profiles (Fig. 1) show clear evidence for remobilization of Zn and Mn near the surface of the microbial mat. The detailed similarity of the Zn and Mn profile strongly suggests that their mechanism of remobilization at the surface of the mat is related. By contrast the Zn and Mn maxima observed in the sediment were not coincident, indicating that their mechanisms of remobilization may be different at this location. The pronounced As maxima within the sediment is clearly separated from those of Zn and Mn. This ability of DGT to resolve remobilization sites for different metals should provide more detailed mechanistic information in future studies. There is some evidence for both Fe and As mobilization at the surface of the microbial mat, ~1 mm above the maxima for Zn and Mn.

At near neutral pH, Fe(II) and Mn(II) are the dominant redox states in solution which will be measured by DGT. The chelex resin binds cations and therefore will measure As(III) rather than As(V) which is present as oxyanions. Although As(OH)₃ is the dominant form in solution, its rapid dissociative equilibration with cationic species allows its measurement by DGT. Coincident As and Fe mobilization has been previously observed¹³. The detailed correspondence of As and Fe at submillimetre resolution within the microbial mat probably reflects reductive mobilization occurring within microniches. It is tempting to attribute the close correspondence of Zn and Mn to release of adsorbed Zn from reductively remobilized manganese oxyhydroxides, as bacteria can rapidly reduce Mn even in the presence of O₂ (ref. 14). However, the data provide no direct evidence of redox regulation and the behaviour of Zn in lakewater columns has been more closely linked to uptake by (and release from) biota than to iron and manganese transformations¹⁵. Alternative hypotheses could include metal release induced by pH changes associated with large and rapid changes in CO₂/O₂ as a result of photosynthesis and respiration.

The x-axes in Fig. 1 show fluxes and concentrations. DGT directly measures fluxes from the pore waters to the resin gel layer. Only if the pore waters are rapidly buffered can the results be interpreted as concentrations. Zn concentrations measured at the same site by conventional DGT at 1 mm intervals, using acid extraction, were shown to be independent of gel layer thickness. This result agrees with measurements in other systems, suggesting that Zn concentrations in pore waters are generally well buffered⁶. Without similar confirmation for other elements, their concentration scales must be treated cautiously. However, the steep concentration gradients observed for Mn and Zn can only be maintained if there is appreciable resupply from solid phase to solution, so for Mn at least, interpretation as a concentration is reasonable.

The image intensity maps (Fig. 2) were only obtained close to the sediment–water interface where concentration gradients are relatively uniform. They show clear horizontal gradients for both Mn and Zn, suggesting that the remobilization of these two elements in the sediment may be related even though their maxima are not coincident. Because of the horizontal heterogeneity, fluxes from the sediment to the overlying microbial mat calculated from concentration gradients will depend on the precise location of any measured concentration profile. There is no clear general relationship between As and Fe in this zone where there is a small concentration gradient and little evidence for active remobilization.

However, a region (~100 μm × 100 μm) with the highest iron measurements is in the same position as the zone of the highest As measurements, again indicating coincident mobilization of As and Fe within microniches.

Concentration gradients and deduced fluxes can only be quantitatively interpreted if measurements are made at sufficient spatial resolution which, in productive systems such as this, is 100 μm. Whether the deduced fluxes are generally representative of the sediment–water interface depend on the presence of horizontal concentration gradients and the temporal nature of the profile. The following geochemical interpretations apply only to the 24 hours during which the DGT measurement was made.

For iron there is no maximum within the surface 7 mm of sediment and a clear concentration gradient from pore waters to the overlying microbial mat is observed. There is similar transport of As, Zn and Mn across the sediment/microbial-mat boundary, but the location of the sub-surface supply is well defined. Clearly the lower part of the microbial mat acts as a sink for metal remobilized in the surface sediment and at the surface of the microbial mat. Microbial mats dominated by cyanobacteria have been shown to produce negatively charged polysaccharide biofloculants capable of binding trace metals¹⁶. It would be interesting to know if their production is restricted to the lower layers of the microbial mat.

Supply of fresh particulate material to the sediment surface is effectively cut off by the presence of the microbial mat. Measurements of Zn in Sankey Brook using 1-mm resolution DGT in March 1996, before a microbial mat was present, showed a much steeper and larger Zn maximum at the sediment–water interface. The mobilization of Zn and Mn at the microbial mat surface (Fig. 1) may simply be due to rapid remobilization of metals from decomposing particulate material landing on and being trapped by the microbial mat, although a more direct participation and control by the microbial community cannot be ruled out. The net effect of the microbial mat is therefore to limit the supply of metals to the sediment while simultaneously trapping any metal remobilized from the sediment. Consequently the amount of metal accumulated in the sediment will be less than it would have been in the absence of the microbial mat. According to these observations microbial mats may be active sites of metal remobilization as well as efficient traps for trace metals.

These measurements of trace metals at unprecedented high spatial resolution reveal geochemical processes occurring on a sub-millimetre scale. They indicate that sources and sinks of trace metals may be very localized, perhaps more so than physiologically driven oxygen gradients which have been elegantly measured by microsensors^{2,3}. Interpretation of metal fluxes and gradients and the role of microniches will be aided by the combined application of DGT and microsensors, particularly planar optrodes, which have provided fine-scale measurement of two-dimensional oxygen distributions⁴. Measurement of oxygen and labile concentrations of Fe(II), Mn(II) and S(–II) by voltammetric microelectrodes¹⁷ would complement the direct measurement by DGT of remobilization fluxes. We are at present developing DGT techniques for phosphate, caesium and sulphide. Combined applications of all these micro-measuring techniques are likely to advance our understanding of solute behaviour at any aquatic interface. □

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Measuring the pulse of a plume with the sedimentary record

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Magmatic underplating associated with mantle plume activity is an important mechanism for driving regional surface uplift and denudation of large portions of the continents^{1,2}. Such uplift occurs rapidly because substantial volumes of basaltic melt are added to the crust over geologically short periods of time (1–10 Myr)², and can lead to large amounts of clastic sediment being shed into surrounding basins³. An intensively studied example of this process occurred in the North Sea basin during the Palaeogene period, where discrete pulses of deposition were triggered when sands were remobilized downslope from the shelf by turbidity currents and debris flows as a result of episodic changes of relative sea level³. Here we correlate the timing of these sediment pulses with the timing of surface uplift inferred to have been caused by episodic magmatic underplating on the continental shelf of northwestern Europe. This magmatism was related to activity of the Iceland plume, suggesting that individual pulses of sedimentation provide a potentially sensitive measure of plume activity, and so may be used to resolve time-dependent fluctuations in mantle plume activity predicted by theoretical studies of mantle convection.

We have chosen to examine the northwest shelf of Europe for three reasons. First, the history of vertical motions has been carefully studied³ over the past 20 years. Second, the distribution, composition, volume and age of onshore and offshore igneous activity are well documented^{4–7}. Third, the biostratigraphy, chronostratigraphy and seismic stratigraphy of Palaeogene sedimentary rocks have been systematically studied using both onshore data and extensive seismic and well data made available by the hydrocarbon industry^{3,8}.

In the Early Cenozoic era, an area encompassing the British Isles ($\sim 3 \times 10^5 \text{ km}^2$) underwent rapid exhumation (Fig. 1). Substantial quantities of Palaeogene muds and sands were deposited in the North Sea and in other basins including the Faeroe–Shetland basin, the Porcupine basin west of Ireland and southeastern England^{9–11}. Marine sedimentation was strongly pulsed, suggesting a pattern of transgression and regression which was first recognized by Lavoisier in 1766. A detailed history of highstands and lowstands of Palaeogene relative sea level in the North Sea basin is now available^{12,13}. These relative sea-level changes are recognizable around the British Isles but their magnitude and timing cannot be correlated throughout northwestern Europe or worldwide¹³. This observation indicates that global (that is, eustatic) sea-level variation did not control the cyclic pattern of deposition. We are especially concerned with the period between 62 and 54 Myr ago when a series of submarine fans formed at intervals of $\sim 1 \text{ Myr}$ on either side of the emergent Scottish landmass. These pulses of sand deposition are well documented in the North Sea and coeval pulses have been recognized in the Faeroe–Shetland basin¹⁴.

Permanent uplift and denudation of a region encompassing the British Isles were triggered by Palaeogene magmatic underplating^{1,15}. Geochemical and subsidence modelling show that this magma was generated by adiabatic decompression of asthenosphere with a potential temperature of 1,450–1,500 °C, requiring the existence of a mantle plume^{4,16}. The existence of a possible 50–250 m of transient dynamic uplift associated with the proto-Iceland plume^{2,17} cannot account for permanent uplift and does not affect our principal conclusions. Assuming Airy isostasy, the amount of magmatic underplating, X , required to generate an amount of denudation, D , is given by

$$X = \left(\frac{\rho_a - \rho_s}{\rho_a - \rho_x} \right) D + \left(\frac{\rho_a}{\rho_a - \rho_x} \right) T + \left(\frac{\rho_a - \rho_w}{\rho_a - \rho_x} \right) W \quad (1)$$

where T is the present-day topography (that is, residual uplift) and W is the water depth during the Late Cretaceous before uplift. Other parameters are given in Table 1. In the Irish Sea, $\sim 2.5 \text{ km}$ of strata have been eroded from extant Permian–Triassic basins and there is little residual uplift. If Late Cretaceous water depths were in the range 200–600 m, the required underplate is $8 \pm 2 \text{ km}$. If the same amount of underplating occurred beneath Scotland where Late Cretaceous water depths were 0–300 m, an average present-day topography of $\sim 500 \text{ m}$ implies that D is 0.5–2 km. This estimate of D is consistent with fission track analyses¹⁸ and with emplacement depths for igneous complexes⁴. If ρ_x is reduced to 2.8 Mg m^{-3} , then $X = 6 \pm 1 \text{ km}$.

Widespread magmatism is manifested at the surface by numerous central igneous complexes, lavas, linear dyke swarms, and other, minor, intrusive bodies (Fig. 1). Although accurate volumetric estimates of magmatism are difficult to make, studies of petrological fractionation support the notion that a substantial volume of magmatic underplating exists (3–5 times the volume inferred from outcrop¹). Large volumes are corroborated by forward and inverse modelling of concentrations of rare-earth elements for basaltic rocks. After corrections for fractional crystallization of the observed melt compositions, these data indicate that $\sim 5 \text{ km}$ of melt was produced at depth⁴. Wide-angle and deep seismic reflection data provide a further important constraint for the amount of underplating². The lower crust beneath the British Isles is strongly reflective and has a Poisson's ratio of ~ 1.86 , consistent with the existence of mafic sills. Beneath Scotland, the Lithosphere Seismic Profile in Britain (LISPB) wide-angle data set shows that P-wave velocity increases sharply at 20 km depth, and that the velocity 5–8 km above the Moho is $6.6\text{--}7 \text{ km s}^{-1}$ with calculated densities of $2.85\text{--}3.05 \text{ Mg m}^{-3}$ (ref. 19). Thus geochemical and geophysical observations are consistent with the underplating hypothesis.

Dating of onshore igneous rocks has proved difficult because of significant argon mobility and most of the published K–Ar ages are

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