

Gas hydrate crystals may help build reefs

During a recent cruise in the Porcupine Basin, off southwest Ireland, we discovered two extensive and hitherto largely unsuspected deep-water reef provinces, including a giant cluster of hundreds of buried mounds. The ring shapes of many reefs suggest that they are caused by an axial fluid expulsion at the sea bed, a transient flow well confined in space and time. We are exploring various hypotheses, but a stimulating avenue for research is opened by a glacially controlled growth pulse and subsequent decay of a shallow layer of gas hydrates as a methane buffer and probably indirectly as a ground for overlying biological communities.

Seismic profiles in the Porcupine Basin had already identified a number of large deep-water carbonate mounds. These are up to 2 km in diameter, with heights of 250 m (ref. 1). Gravity cores on the mounds recovered deep-water colonial coral debris (*Lophelia* sp.), identical to the fauna collected by Wyville Thomson in the area during HMS *Porcupine's* cruise in 1869 (ref. 2). A high-resolution seismic survey with R/V *Belgica* in May 1997 revealed that these large isolated seabed mounds are only one of several reef types in the basin. The large mounds are flanked to the north by a 1,200 km² province of smaller reefs, 50–100 m in height, covered by a few tens of metres of sediments

(Fig. 1a, b). These are the Magellan reefs, named after the survey vessel that had observed them a few months earlier. The large surface reefs seem to be associated with fault-controlled methane seeps from deeper hydrocarbon reservoirs¹, but the numerous buried reefs, rising from, or rooted to, a common and virtually undisturbed geological horizon, do not show any obvious correlation with deeper faults. Reflection seismograms of the Magellan reefs reveal the widespread twin associations of symmetric lung- or butterfly-shaped structures, suggesting central cross-sections through ring structures (Fig. 1a, c).

Such ring reefs call for an axial causal mechanism. Singular methane vents or mud volcanoes could have been girdled with 'stone rings' of reef-building communities. There is still a poor understanding³ about whether chemosynthetic and symbiotic communities^{4,5} that could contribute to reef-building processes benefit directly from the seeping gases, or whether deep-sea reef construction in seep environments is simply a matter of preferential settlement and growth on solid, authigenic carbonates, which have been widely reported as primary deposits fringing seep sites⁶.

The sudden onset and near-synchronous decay of the well-confined, giant Magellan mounds province with its numerous ring reefs implies a regional and transient degassing event, not fully compatible with the pace of deeply rooted geological processes. Here a palaeoclimatic control can be invoked. Environmental and spatial argu-

ments indicate the possible mediating and buffering role of a shallow methane hydrate reservoir, which might have grown and spread widely upslope from discrete deep feeder pipes, particularly in glacial times, when the Porcupine sea bed was swept by colder bottom currents. The upslope boundary of the Magellan province, where the reef structures fade out, follows depth contours of the sea bed (Fig. 1b), supporting the idea of a pressure control on the extension of the hydrates. When such a hydrate layer, usually capping a reservoir of free gas, subsequently decayed and cracked in warmer postglacial waters, it could have funnelled methane over hundreds of seeps to the sea bed.

Gas hydrates are ice-like crystalline compounds that occur when water molecules form a cage structure around guest molecules under conditions of high pressure and low temperature, which are mostly found in the marine environment below water depths greater than 500 m (ref. 7). Their generation generally requires the presence of a prolific methane source. The occurrence of gas hydrates on various margins of the oceans, mostly associated with hydrocarbon seeps, is being increasingly demonstrated; their relevance to world margin stability, the marine biosphere and climate is of significant topical relevance. Although other possible models are being explored, the methane hydrate mediation hypothesis, if verified, would shed new light on the interaction between submarine gas seeps and a climate-controlled interplay between seabed gas hydrates and the deep ocean biosphere.

Still another, fundamentally different, reef setting has been discovered on the eastern margin of the Porcupine Basin: huge barrier-like reefs with ponded sediments, rising from an enigmatic, acoustically transparent and deeply eroded sole layer, which seem to fringe a buried, fossil shelf edge at water depths of about 750 m (Fig. 1e). This is reminiscent of Nordic settings⁸ of small cold-water reefs on shelf breaks, where hydrodynamic conditions (internal waves) and nutrient fluxes shape preferred sites for suspension-feeding communities.

Such discoveries indicate that the Porcupine Basin is a major deep-water coral reef province, while highlighting some hitherto unsuspected habitats of reef-building communities in deep, cold waters. They provide a potential hydrocarbon indicator in a petrolierous basin in the North Atlantic, illustrate a range of deep-water carbonate habitats and provide clues to the Late Tertiary and recent evolution of the basin.

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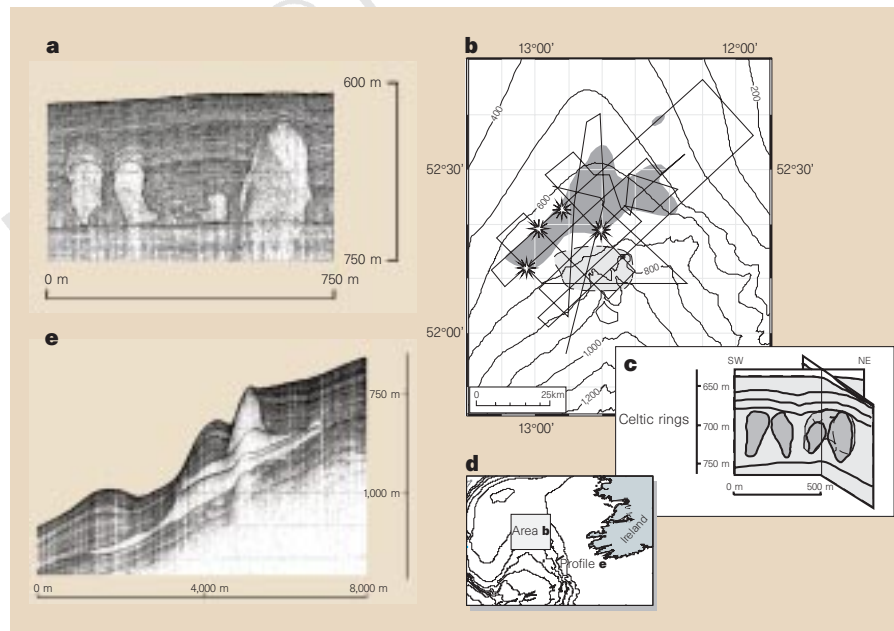


Figure 1 Magellan reefs. **a**, Illustrative seismogram of a central cross-section through a small buried ring reef (left) and a slant section through a larger ring reef, buried below about 30 m of sediments. **b**, R/V *Belgica* track map and outline of the Magellan reef province (black), north of the occurrence of large surface mounds (area circled by dotted line). A few buried reefs that reach the surface are indicated by stars. Bathymetry is contoured in metres. **c**, Line drawing of cross-sections of ring reefs on intersecting profiles. **d**, Location of map (**b**) and profile (**e**). **e**, The barrier-like 'Belgica reefs' fringing a buried shelf edge on the eastern slope of the Porcupine Basin.

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Role for lichen melanins in uranium remediation

Lichens are successful colonizers in extreme terrestrial habitats world-wide, including metalliferous environments¹. Their ability to accumulate metals has led to their use in monitoring radionuclide fall-out from Chernobyl and uranium uptake from dust resulting from mining². Here we report for the first time a lichen growing directly on uranium minerals and uranium being concentrated within its tissues. Our study suggests that melanin-like pigments, substances previously unreported within lichens, are involved.

We discovered the lichen *Trapelia involuta* growing directly on the secondary uranium minerals metazeunerite ($\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$) and metatorbernite ($\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) on uraniumiferous spoil heaps in Cornwall³. X-ray element maps for uranium across transverse sections through the lichen–rock interface show uranium accumulation principally within the outer fruiting body (apothecia) walls of the lichen compared with their interior (Fig. 1a, d). These high uranium concentrations are not caused by the trapping of mineral particles, as reported in previous studies, because U-to-Cu, U-to-As and U-to-P ratios within the lichen differ significantly from those of possible trapped mineral phases. Complexing with oxalic acid and secondary lichen products can also be discounted as mechanisms because we identified calcium but no uranium-bearing oxalates within the apothecial walls. We irrigated sections with the oxidizing agent sodium hypochlorite, confirming the presence of the secondary metabolite

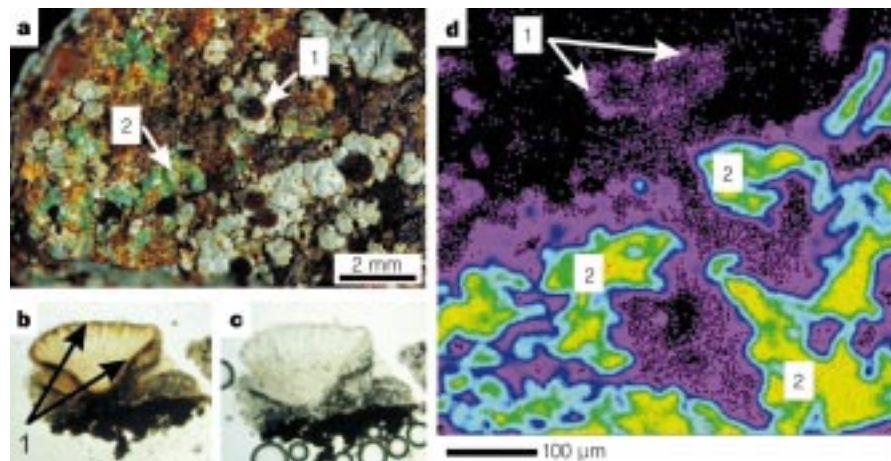


Figure 1 Lichen concentrating uranium. **a**, *Trapelia involuta* (1) with dark brown apothecia growing on metazeunerite ($\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$) (2); **b**, transverse section of *T. involuta* apothecia showing pigmented wall, without treatment with sodium hypochlorite; **c**, the same section with wall decolorized by irrigation with sodium hypochlorite; **d**, X-ray element map showing uranium accumulation (1) in apothecia wall of *T. involuta* growing on metazeunerite (2).

gryphoric acid within the main lichen body, but not within the apothecia, suggesting that this is also not responsible for the uranium accumulation.

Trapelia specimens present on uraniumiferous spoil have atypically dark brown–black (rather than pale red–brown⁴) apothecia, the pigment being restricted to their outer walls and visible in thin section (Fig. 1). Melanin is known to form in non-lichenized fungal hyphae as a response to a wide range of environmental stresses, including metal contamination⁵. We therefore extracted the pigment⁶ from about 100 *Trapelia* apothecia. Fourier transform infrared spectra of the dark pigment indicated the presence of aromatic organic compounds similar to humic acids⁷. This, together with the observation that the dark pigment is decolorized by sodium hypochlorite (Fig. 1b, c), suggests that the compound is melanin or melanin-like. In the samples studied, there is a strong correlation between the localization of melanin and high concentrations of uranium, which agrees with experimental studies⁶ showing that melanin has a high adsorption capacity for uranium. It is possible that melanization in *T. involuta* is an adaptive response to protect the ascospores, the sexual reproductive bodies formed within the apothecia, from the toxic effects of the uranium.

Our findings are an important step towards enhancing the use of lichens as biological monitors of radionuclides and potentially in remediation processes. Laboratory studies on yeast and fungal biomass have shown effective uptake of uranium, leading to the biological treatment of metal-contaminated effluents. In a pilot study⁸, pellets of the non-lichenized fungus *Aspergillus niger* were used successfully in a fluidized-bed reactor for the removal of uranium, a process 14 times more effective than a commercial ion-exchange resin. The ability of lichens to

concentrate metals from solution is also demonstrated by the development of a biosorbent based on immobilized lichens⁹. Because lichens grow slowly, it is unrealistic to expect them to be used directly in bio-remediation programmes to concentrate metals. However, mechanisms of bioaccumulation are poorly understood in microorganisms, and lichenized fungi have an important role. Specific lichen tissues have been shown to concentrate secondary metabolites to more than 20% dry weight¹⁰. Localization and characterization of organic metal compounds in organisms are a major challenge for analysts; the capacity for lichens to accumulate such high concentrations makes them model systems for studying fungus–metal interactions.

Other lichen species in uraniumiferous environments must now be studied, to allow us to assess the wider response of lichens to uranium. Other species might concentrate uranium to far higher concentrations and by different mechanisms. By identifying how lichens accumulate uranium, remediation technologies based on these mechanisms might be developed.

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