



Figure 1 A coyote in southern California, photographed by a remotely triggered camera. Crooks and Soulé² found that bird diversity is higher in fragments of southern Californian sage bush where coyotes are present, as they reduce the number of smaller, bird-killing predators.

habitat fragment decreased significantly as the abundance of coyotes rose, and was highest in small fragments where none were present.

Finding a negative relationship between the abundance of coyote and mesopredators does not, however, prove that there is a direct negative interaction between the two groups of species. The fragmentation process could improve habitat quality for mesopredators, leading to their abundance increasing independently of the loss of coyote. But by analysing the variation in coyote abundance across time within single fragments, Crooks and Soulé were able to provide evidence for a causal relationship. The mesopredators, especially cats, reduced their use of fragments when coyotes were present. Furthermore, coyotes often killed cats. This suggests that mesopredators actively avoid coyotes to reduce the risk of becoming prey.

The changes in the structure of the carnivore community, which were caused by habitat fragmentation, strongly affected the composition of the bird community — as predicted by the mesopredator-release hypothesis. When coyotes became rarer in a fragment, the diversity of bird species decreased, probably because of more efficient predation, especially by cats. The decrease was larger in older fragments. These results are a good illustration of a general principle in conservation biology: it takes a relatively long time to properly assess the impact of human interference on ecosystems.

Crooks and Soulé's study² is an important addition to a small, but exclusive, list that lets us see how changes in the composition of carnivore communities affect species at lower trophic levels. Although based on very few studies, these complicated indirect effects seem to be more of a rule than an exception. For example, when red fox populations in the

boreal forests of northern Europe were greatly reduced by an outbreak of sarcoptic mange during the late 1970s and the 1980s, the number of pine martens shot up, most likely because fewer were killed by foxes⁵. The reduction in the fox population was also associated with an increase in the population density of mountain hares and grouse⁶. Similarly, there is experimental evidence that the species composition of the predator commu-

nity strongly affects the way the prey population fluctuates through time⁷.

Large predators get a mixed press. Many hunters consider them as a severe competitor for ungulates, such as deer. However, if Crooks and Soulé's results represent a general pattern they caution against simply labelling the ecological effects of a species as 'good' or 'bad'. For example, we can only speculate whether the replacement of the red fox as the top predator in many Scandinavian boreal ecosystems by the rapidly expanding grey wolf population will lead to lower fox densities, resulting in more hare and grouse because of reduced predation by foxes. The reintroduction, or unfortunate disappearance, of top predators provides a unique opportunity to study complex trophic interactions. The ecological consequences are very hard to predict, but they are likely to be considerable. □

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Oceanography

An ultimate limiting nutrient

J. R. Toggweiler

Several elements in the ocean — most notably nitrogen, phosphorus, iron and silicate — are essential for the growth of phytoplankton. Like fertilizers applied to the land, the supply of N, P, Fe and Si in seawater upwelling from below, or in airborne dust deposition from above, determines the rate of production of new organic matter at the surface. It is unlikely, however, that all four elements are equally limiting to growth. Is one clearly more important than the others and, if so, on what timescales? On page 525 of this issue¹ Tyrrell makes a strong case that it is phosphorus, in the form of dissolved phosphate (PO_4^{3-}), that is the ocean's 'ultimate limiting nutrient'.

Of all the nutrients in the ocean, PO_4^{3-} has the longest residence time at around 50,000 years². Residence times of the other nutrients are much shorter — 5,000 years for NO_3^- (nitrate)³, 15,000 years for SiO_2 (silica)⁴ and perhaps 30 years for Fe. Phosphate enters the ocean in rivers, as a product of continental weathering; it is lost from the ocean by being buried in sediments. But like Houdini, PO_4^{3-} is remarkable in its ability to escape burial. Only 1% or so of the upwelled phosphorus

taken up by phytoplankton is trapped in sediments⁵. So, considering its rate of input and output from the system, the marine standing stock of PO_4^{3-} is fairly large.

Much of the recent interest in ocean nutrients has centred on the fast-throughput nutrients NO_3^- and Fe which have relatively low stocks in relation to their delivery to the system. Addition of NO_3^- and Fe has been shown to increase phytoplankton biomass dramatically (see ref. 6 for instance). Tyrrell's work makes us appreciate that these dramatic effects are relatively short lived; on long timescales, it is the PO_4^{3-} content of the ocean that sets the standing stocks of the other nutrients.

Tyrrell set himself the goal of building a simple model to describe the relative abundances of NO_3^- and PO_4^{3-} in the ocean. The model is based on the ecological competition between two types of phytoplankton, those that can fix N_2 from the air ('nitrogen fixers') and those that cannot. The nitrogen fixers have an advantage in growth rate when nitrate is scarce, but are limited by a lower growth rate when it is abundant. Tyrrell assumes that both kinds of phytoplankton

construct their biomass with an N:P ratio of 16:1, the so-called Redfield ratio. His model then reproduces the covariance between NO_3^- and PO_4^{3-} observed in sea water, a simple linear trend with a slope of about 15:1 (see Fig. 1 on page 525). The model produces a slight excess of PO_4^{3-} in surface waters when all available NO_3^- has been consumed. This prediction is supported by observations which show that surface sea water often contains low, but non-zero, concentrations of PO_4^{3-} alongside zero NO_3^- . This slight excess makes nitrogen sufficiently limiting that Tyrrell's nitrogen fixers are at an advantage.

The $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio of sea water is smaller than the N:P ratio in phytoplankton biomass because there is a very large sink for NO_3^- in the ocean's interior due to denitrification, the consumption of NO_3^- and production of N_2 by bacteria in areas where oxygen is not present⁷. When denitrification draws the $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio in the surface ocean down to a level where Tyrrell's nitrogen fixers can compete successfully with the non-nitrogen fixers, the production of new NO_3^- by the nitrogen fixers rises to balance the denitrification sink.

The central point to come out of Tyrrell's model is a prediction that the balance between nitrogen fixation and denitrification is ultimately set by the river input of PO_4^{3-} ; more PO_4^{3-} input leads to more denitrification, which in turn leads to more nitrogen fixation. The nitrogen cycle, being more adaptable than the phosphorus cycle, adjusts to the input and loss of the more limiting nutrient. The fact that the most limiting nutrient has the longest residence time in the ocean implies that the ocean is fairly well buffered against sustained changes in nutrient stocks.

Perhaps the most contentious aspect of

Tyrrell's model is that it makes no provision for an important role for Fe. Nitrogen fixers are known to have a large appetite for Fe, and it is widely thought that the rate of nitrogen fixation is at least locally influenced by its availability from atmospheric dust^{8,9}. In the context of Tyrrell's model, however, the global rate of nitrogen fixation cannot be dependent on the input of an element such as Fe which has a short residence time. This is because a sustained pulse of Fe input leading to increased nitrogen fixation would simply 'mine out' all available PO_4^{3-} from the upper ocean, leading to curtailed phytoplankton production.

From the latest work on Fe cycling, it seems that the residence time of total Fe in the ocean may not be as short as previously believed. Some as-yet-unknown process appears to bind Fe to organic ligands so that it is present in subsurface sea water in much larger quantities than expected from the scavenging kinetics of the naked ferric ion¹⁰. Indeed, it may turn out that organisms alter the cycling of Fe in such a way that in the ocean it is regulated by the river input of PO_4^{3-} , just like NO_3^- . □

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almost exclusively of the ^4He isotope, but there is another stable isotope, ^3He , a by-product of the production of tritium in nuclear reactors, which has quite different quantum characteristics. This rare isotope has also been extensively studied, both alone and in the form of ^4He – ^3He mixtures (the two isotopes are partially soluble in each other⁵).

Polturak and his team have studied solid ^4He – ^3He 'alloys' (their term) by using nuclear magnetic resonance (NMR). The basic measurement here is the 'motional narrowing' of the NMR resonance line of ^3He , which allows the speed of diffusion of this isotope to be assessed. Over a narrow temperature range, the helium 'alloy' consists of a mixture of solid plus superfluid in equilibrium, and, because the two phases are of different isotopic composition, the two He isotopes can be regarded as distinct components (at least in terms of the phase rule). Three years ago⁴ Polturak's group made the surprising discovery that the mobility of ^3He in the solid is higher than in the superfluid. No other solid is known in which atoms move faster than in the melt at the same temperature: we have here a remarkable case of superdiffusion, to add to the other 'super' characteristics of helium at low temperatures. It turns out that the solubility of ^3He in ^4He increases hand in hand with the appearance of crystal vacancies — the authors suggest that the ^3He is attracted to vacancies because ^3He has a larger zero-point vibration than ^4He , and so should migrate preferentially into a vacancy. Something similar had been deduced some years ago⁶ from the anomalously fast motion of Sn impurities in solid Pb.

In two sets of experiments^{1,2}, Polturak's group observed slow plastic flow (creep) in single crystals of solid ^4He and of ^4He – ^3He mixtures. Stress was imposed on the solid helium (without any heating) by passing a current through a superconducting metal wire embedded in the crystal in the presence of a magnetic field. The diffusion of vacancies and the counterflow of atoms allowed the wire to move through the crystal (Fig. 1a). A separate coil was used as a sensor to measure the rate of movement of the wire, and velocities as low as 10^{-8} mm s⁻¹ could be measured. For low stress, the creep rate was proportional to the imposed stress, and this is consistent with deformation by the well-established Herring–Nabarro mechanism, also called 'vacancy creep' (Fig. 1a).

The velocity of the wire through a pure ^4He crystal reaches a very high peak due to superdiffusion at the exact temperature at which the h.c.p structure changes to b.c.c. (Fig. 1b)¹. (Various tests prove that the phase transition and the diffusion peak coincide within 1 mK.) Similar maxima, though far less extreme, are seen in b.c.c. metals such as Ti, and have been attributed to the so-called

Materials science

Superdiffusion in solid helium

Robert W. Cahn

Low-temperature physics is a field that can appear sealed off from much of the rest of science, and metallurgy in particular. Its practitioners think in terms of millikelvins rather than, like metallurgists, in thousands of kelvins, and observe strange quantum-linked phenomena such as superfluidity and superconductivity. But when a group of low-temperature physicists — in this case, Emil Polturak and colleagues at the Technion in Israel — focus, exceptionally, on the mechanical behaviour of solid helium their results hold particular interest for metallurgists^{1–3}. Following on from their discovery of unusually rapid diffusion in solid helium⁴, Polturak and co-workers have shown that this 'superdiffusion' occurs at the exact temperature at

which solid helium changes crystal structure¹ and is linked to a reduction in resistance to stress at this temperature². In a computer simulation³, they relate this anomalous behaviour to a new theory of melting. This work covers a whole range of phenomena normally studied by metallurgists, but all within one or two kelvin of absolute zero.

Helium cannot be solidified at ambient pressure, but at pressures exceeding 25 atmospheres and below about 2.5 K it can be turned into a hexagonal-close-packed (h.c.p.) crystal. Over a narrow range of pressures and temperatures near 30 atmospheres and 1.8 K, this structure changes allotropically to a body-centred cubic (b.c.c.) form⁵. Natural helium consists