Gold’s catalytic properties seem to depend less on the material on which it rests for liquid-phase oxidation than they do for gas-phase oxidation. However, the support material might be expected to influence at least the dispersion of the gold and thus its catalytic activity. The efficacy of gold nanoparticles as catalysts is also markedly enhanced when the particles are less than 6 nanometres in diameter. Those used by Hutchings and colleagues were relatively large, with mean diameters of around 25 nanometres, making further improvement in catalytic performance distinctly possible. Future investigations on the effects of size and support material may well reveal a far wider scope for catalysis by gold.

Exactly how gold particles activate molecular oxygen at such low temperatures remains unclear. It is equally uncertain how epoxidation works; this is the oxidation method favoured by industry but which, chemically, is the least probable route to the oxidation of hydrocarbons. Convincing answers to such questions would provide us with a valuable roadmap for pursuing green, sustainable chemistry through control of the reactivity of oxygen—which is just how enzymes act.

Gold has long been held in the imagination as a thing of never-changing beauty and value. Now it might hold our imagination as an instrument of change at the nanometre scale.

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EVOLUTION

Along came a sea spider

Graham E. Budd and Maximilian J. Telford

An investigation of brain development in sea spiders provides hints about how the earliest arthropod head evolved. These observations are bound to provoke controversy in an already acrimonious field.

Obscure groups of animals have been making scientific waves lately, and few are more obscure than the sea spiders, or pycnogonids. These marine, spider-like animals differ from other arthropods, such as the true spiders, crustaceans and insects, in many ways. Their bodies are so slender that the digestive systems and gonads are squeezed into their limbs; they possess a forward-pointing proboscis with a terminal mouth; and the males brood the eggs. Flanking their unique proboscis is a pair of pincer-bearing appendages known as chelifores, which it has long been assumed are related to the pincered fangs — chelicerae — of spiders.

Work presented by Maxmen et al. on page 1144 of this issue, however, suggests that pycnogonid chelifores and spider chelicerae develop from different regions of the head and therefore cannot be equivalent. At first sight this is a rather esoteric finding. But if it is correct, it will shake up the field of arthropod evolution.

Maxmen et al. relied on the fact that each of an arthropod’s pairs of appendages is derived from one of the repeating segments that make up the arthropod body. In addition to its appendages, each segment has a pair of nerve concentrations, or neuromeres. The authors reason that tying the appendages to a specific pair of neuromeres should reveal which segment the appendages belong to. As chelifores and chelicerae are head appendages innervated from the brain, Maxmen et al. considered which of the brain neuromeres each appendage is associated with during larval development. Arthropod brains are divided into three regions: protocerebral, deutocerebral and tritocerebral, from front to back. The anterior-most appendage of most living arthropods, including the spider chelicera, is innervated from the deutocerebrum. What Maxmen et al. have now shown, in surprising contrast, is that the pycnogonid chelifores seem to be innervated from the protocerebrum — the most anterior part of the brain. The association of chelifores and chelicerae with different parts of the brain implies that the two types of limb are not equivalent, but are derived from different segments.

This result cuts across previous results based on adult structure, and to see the wider implications we need some historical background. The composition of the arthropod head is one of the bitterest and longest-running problems in animal evolution. Unresolved after more than a century of debate, this sorry tale is (in)famously known as the “endless dispute”.

Much of the attention in this dispute has been directed towards the nervous system. It is widely agreed that the deutocerebrum, tritocerebrum and the more posterior parts of
the nervous system are derived from successive segmental neuromeres. The deutocerebrum innervates the antennae of insects, the anterior antennae of crustaceans and the cericerae of spiders and scorpions. But the real meat of the endless dispute has always concerned the nature of the appendage-less front-most part of the brain, the protocerebrum. Is it some sort of non-segmental leftover inherited from the very earliest animal ancestors of the arthropods (a mystical structure called the acron in the literature), or does it represent the neuromere of a once appendage-bearing anterior segment?

Two lines of evidence have been put forward in support of the existence in ancient arthropods of a protocerebrum with an appendage. First, all extant arthropods (except pycnogonids) possess a small, appendage-like outgrowth of the body which lies just in front of the mouth and is called the labrum. Confusingly, the labrum is not innervated by the protocerebrum (fanning the flames of the dispute); however, in the embryo it starts off right at the front of the animal, and migrates backwards during development. If the labrum represents a highly modified appendage, then its anterior position in development might indicate that it is the long-sought limb of a protocerebral segment.

Second, there is the fossil evidence of the earliest arthropods from 530–490 million years ago. Many of these early arthropods possessed a pair of large, grasping or branched appendages, known as the ‘great appendage,’ found at the anterior of the head. Indeed, a phylogenetic reconstruction published a few years ago suggested that the great appendage was innervated from the protocerebrum. We cannot investigate the nervous system of a fossil, however, and this reconstruction has been hotly disputed, with many researchers preferring to see the great appendage as equivalent to the antennae of insects and crustaceans.

However, if, for the sake of argument, we accept these two lines of evidence at face value, we could reasonably conclude that the protocerebral appendage started out as a great appendage that has subsequently shrunk to the small nub of tissue we now see in most living arthropods as the labrum.

The wider significance of the conclusions of Maxmen et al. now becomes clear. The presence of a bona fide appendage on the pycnogonid protocerebrum (and the absence of a labrum) gives support to the protocerebral origin of the great appendage and to the idea that the labrum is the remnant of this ancient appendage. More excitingly, it implies that the pycnogonids are extraordinary living fossils, retaining an organization of their head that all other living arthropods lost hundreds of millions of years ago.

How, then, might we test these new results? First, we would like a way to verify the association of chelifore with protocerebrum. One way to achieve this would be to use domains of gene expression as segmental markers. Hox genes are especially useful in this regard, as they have relatively stable domains of expression along the anterior–posterior axis of arthropods. This approach has been used successfully to line up the head segments of arachnids and insects, for example. Thus, the anterior-most expression of the Hox gene Deformed (Dfd) marks the fourth segment in both arachnids (Fig. 1a) and insects. Because the arachnid/insect first segment has no associated appendage, this Dfd expression in the fourth segment lines up with the third appendage. If the traditional interpretation of pycnogonid appendage assignment is correct, the anterior-most appendage — the chelifore — will be associated with the second segment and, as in arachnids, the fourth-segment expression of Dfd will therefore be seen in the third appendage of the pycnogonid larva (Fig. 1b).

But if Maxmen et al. are correct, the chelifore comes from the first segment and, counting backwards, Dfd expression in the fourth segment will therefore be seen in the fourth appendage rather than the third (Fig. 1c).
The second avenue is phylogenetic. The evolutionary scheme we have outlined implies that the transition from great appendage to labrum happened once in the common ancestor of all living arthropods apart from the pycnogonids, which must therefore be very basal in evolutionary terms. But if the pycnogonids truly are the sister group of the spiders and scorpions (which some molecular data suggest*), then the results of Maxmen \textit{et al.} will be hard to square (Fig. 2). Testing the phylogenetic position of pycnogonids is therefore crucial.

The conclusions of Maxmen \textit{et al.} overturn entrenched ideas about the body plan of the sea spiders and, furthermore, lend support to some controversial theories of arthropod evolution. Unlike their terrestrial analogues, sea spiders lack a poisonous bite, but this paper is bound to inject venom into what is already one of the most controversial of all zoological topics.

\section*{QUANTUM PHYSICS
Atom waves in passing
Maarten DeKieviet and Joerg Schmiedmayer
Matter-wave interferometers are unique tools for exposing particles acting like waves — one of the stranger facets of quantum theory. They can even measure the quickening of an atom’s ‘pulse’ as it flies past a surface.

Particles sometimes act like waves, and waves sometimes act like particles. This phenomenon, known as wave–particle duality, may seem to confuse what are (to everyday experience at least) two separate and unambiguous concepts. But 100 years after Albert Einstein first introduced the idea of waves behaving like particles to explain the photoelectric effect, and more than 80 years after the French physicist Louis de Broglie proposed the converse behaviour, wave–particle duality has become a staple food of the quantum diet. Writing in \textit{Physical Review Letters}¹, John Perreault and Alexander Cronin expose a further experimental manifestation of the effect, by measuring the shift in phase — a wave property — of an atom as it flies past, and interacts with, a surface.

In doing so, they take advantage of matter-wave interferometry, a technique that has in recent decades given fresh impetus to studies of the wave-like nature of particles. Pioneered for simple particles such as electrons² and neutrons (ref. 3 and references therein), the technique has since been extended to larger particles such as atoms and molecules (ref. 4 and references therein).

Interferometry as a generalized technique involves the superposition of two waves to gain information about their relative phase — where in their cycle they are in relation to each other. A simple analogy is a zip-fastener: for proper zipping, the teeth of one strand must fit perfectly with those of the other. If, however, they are shifted such that the teeth oppose each other, the zipper won’t close. Analogously, if the peaks of one wave are next to the troughs of the other, the waves are perfectly out of phase, and their amplitudes cancel out — they interfere ‘destructively’. Conversely, if the two waves are perfectly in phase, with the peaks and troughs matching, they interfere constructively to produce a net amplitude that is the sum of the two individual amplitudes.

In an interferometer, an incoming wave is split into two branches. One of these branches is subjected to an outside influence that slows down or speeds up the atom-wave’s cycle, or pulse, thus shifting its phase relative to that of the other branch. These two branches are then brought back together and interfere, the amplitude of the resulting wave being proportional to the degree to which the two waves are in phase. Generally in wave mechanics only intensities — the squares of the amplitudes — can be measured, so phase information is lost. The power of interferometry is that it transforms a shift in phase to a change in amplitude, which can be measured as change in intensity.

And so it is in Perreault and Cronin’s experiment¹. They make use of a Mach–Zehnder interferometer, in which a nanoscale grating is used to diffract atomic waves, thus acting as a matter-beam splitter³. The authors inserted a further 250-nm-thick membrane with thousands of 50-nm-wide slits into one branch of this interferometer. As they pass through this additional membrane, the atoms experience a weak, attractive van der Waals force through electronic coupling with the membrane’s walls. This interaction speeds up the atoms’ pulse — the phase of the atom-wave becomes shifted with respect to the free-atom wave in the interferometer’s other branch. From the measured interference, the phase shift caused by the atom–surface interaction can be exactly quantified.

This measurable change in the interference pattern arises from an atomic interaction that occurs over a distance up to 1,000 times that of an atomic diameter. Perreault and Cronin are, to their knowledge, the first to determine directly the phase shift caused by the van der Waals interaction between an atom and a surface. The acceleration towards the surface of the channels experienced by the sodium atom-waves is more than a million times that caused by Earth’s gravitational field. The channels are, however, very short, so the actual time difference measured by the interferometer is only about 100 attoseconds (10⁻¹⁸ seconds). Contrasting this with the overall flight time through the device of around one millisecond gives an idea of the exquisite sensitivity possible with interference experiments. This experiment is a beautiful example of the many tools that are being developed in a true renaissance in the study of atom–surface interactions⁴.

The potential impact of such work stems from its connection to the fields of nanotechnology and atom optics. Nanometre-scale structures could lead to smaller transistors and motors, or the ability to assemble molecules atom by atom. Exploiting the wave behaviour of atoms could lead the way to more precise gyroscopes for navigation, gravity gradiometers for subterranean mapping and other field sensors. The work of Perreault and Cronin lies at the intersection of these two fields, putting a limit on how small nanotechnological and atom-optical devices can be made before the van der Waals interaction disrupts their operation.

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