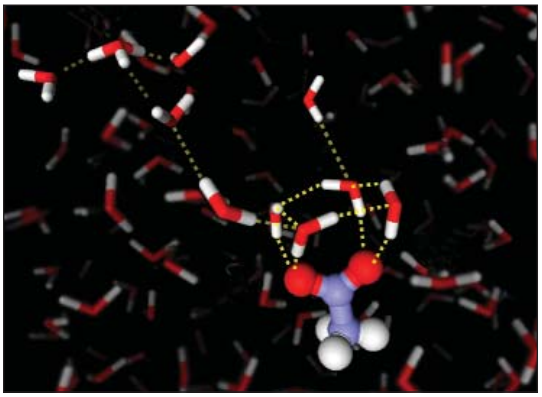
ing liquid. But the ClO_4^- ion is known to increase the macroscopic viscosity of aqueous solutions. This paradox is resolved by noting that a larger effective radius of the ions would account for the increased viscosity (*4*). The required radius corresponds nicely to the size of the ion and its associated hydration shell. Thus, the hydration shell seems to act like a chemically distinct species whose overall size controls the macroscopic viscosity.

The localized character of the hydration shell around a solute anion naturally raises the important question of its molecular structure. Recent studies (*5*) of ions surrounded by a controlled number of water molecules have shed light on this issue. For example, Robertson *et al.* (*6*) have identified the intrinsic structures of the hydration shells around the hydroxide and fluoride ions, and have started to map how water interacts with complex anions such as acetate (see the figure) (*7*). These organic species are more challenging because they possess both hydrophilic and hydrophobic domains (*3*).

Water structure also plays a key role in the kinetics of acid-base reactions. Rini *et al.* (*2*) present an elegant ultrafast study of a photoinitiated proton transfer between an anionic proton donor and the acetate-ion proton acceptor. With a universal infrared probe, the authors can independently monitor the decay of the photo-acid and the rise of both its conjugate base and the acetic acid product. They thus provide an unusually complete picture of how all species in the reaction evolve.

The resulting time profiles clearly differentiate between reactions that occur through initially hydrogen-bonded reactant pairs and those that occur by diffusion of the reactants to form a collision complex. At low concentration, Rini *et al.* observe a third pathway, in which the photo-acid donates a proton to the water molecules in the hydration shell to form the hydronium ion. This species then migrates to find and neutralize the acetate ion long after the appearance of the photo-acid's conjugate base. Water thus plays an integral role in the reaction by shuttling the proton between the reaction partners.



Water in action. Schematic illustration of how the hydration shell around the anionic part of the acetate ion participates in the reaction with H_3O^+. Rini *et al.* (*2*) provide evidence for this proton shuttle mechanism. Omta *et al.* (*1*) show that the effect of an anion on water structure is highly localized.

The two studies (*1*, *2*) illustrate how detailed mechanistic insights into aqueous processes can be obtained with ultrashort time resolution, which allows researchers to look beneath the averaging inherent in bulk measurements. Together with cluster studies, these ultrafast techniques provide rigorous tests of widely accepted molecular-level pictures (*8*, *9*).

One of the longstanding challenges in aqueous chemistry, raised by the work of Rini *et al.*, is the molecular-level mechanism of proton transport (*8*, *10*, *11*). An important step toward this goal is to extend the ultrafast infrared methods demonstrated in the bulk studies reported here (*1*, *2*) to the cluster regime. The advantages of the small systems are that the reactions can be initiated with precisely controlled energy and starting geometry, and the dynamics can be treated with the powerful theoretical tools refined in the study of molecular photochemistry.

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PALEONTOLOGY

Making the Best of a Patchy Fossil Record

Andrew B. Smith

Paleontologists have been striving to document the history of species diversity through geological time for nearly 150 years. Until recently, the favored method involved nothing more complex than counting the fossils recorded from each time interval, and a great effort has gone into compiling taxonomic and stratigraphic data to quantify diversity trends through time.

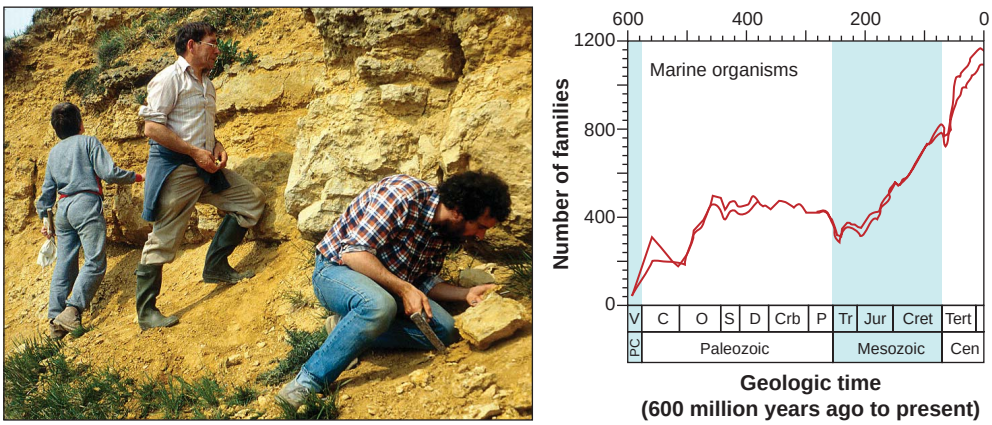
However, this simple approach comes with a price: It is only valid if each time interval has been sampled to the same extent. On page 358 of this issue, Crampton *et al.* (*1*) show that this may not be the case. Working from a massive database of fossil marine molluscs and fossil localities in New Zealand covering the past 60 million years, they point out that sampling effort is far from uniform. Furthermore, sampling effort correlates with the amount of rock that crops out at the surface.

Paleontologists have long been aware that the more thoroughly a rock unit is sampled, the more specimens are found. This, in turn, leads to higher recorded diversity: All other things being equal, if only a small amount of rock is present at outcrop, then the total diversity recorded is likely to be much lower than if a large area of outcrop is available for sampling.

Rarefaction, a statistical technique that uses subsampling to reduce populations to the same size, can be used to remove such bias. Initial large-scale studies with this approach (*2*) suggest that global biodiversity patterns may indeed be substantially biased by unequal sampling. However, rarefaction requires more data than are generally available in global taxonomic compilations. Hence, more indirect ways of estimating sampling levels are required. Two have recently been used.

First, estimates of how extensively a time interval has been sampled have been based on the number of named geological formations (that is, mappable units of rock laid down in a distinct past environmental setting). The more geological formations that are recorded in a time interval, the greater the range of environments that exist to be

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Fossil alert. Paleontologists sample the available rock record efficiently (**left**), but are there biases in the rock record that can distort marine biodiversity curves such as that of Benton (**right**) (*5*)? PC, Proterozoic; V, Vendian; C, Cambrian; O, Ordovician; S, Silurian; D, Devonian; Crb, Carboniferous; P, Permian; Tr, Triassic; Jur, Jurassic; Cret, Cretaceous; Tert, Tertiary. The Paleozoic ran from 544 to 251 million years ago, the Mesozoic from 251 to 65 million years ago, and the Cenozoic (Cen) from 65 million years ago to today.

sampled—and, presumably, the greater the potential species diversity. This relation seems to hold for North America (*3*), but Crampton *et al*. find no correlation between formation numbers and sampling intensity or species diversity in New Zealand. The reason may be that for the past 60 million years, New Zealand and North America have lain in very different tectonic settings, the former part of a tectonically active margin, the latter a stable cratonic platform.

Second, sampling intensity has been correlated with the area of rock available at outcrop for collecting: The larger the surface area at outcrop, the greater the opportunity for collecting—and the larger the collection made, the greater the overall diversity. With this approach, Crampton *et al.* find a strong and significant correlation, but only for the long-term trend and not for short-term changes. They conclude that rock outcrop area is the more reliable predictor of sampling bias in the fossil record (*1*).

However, there are additional complicating factors. Crampton *et al*. show that it is not just the amount of outcrop available to sample that affects taxonomic diversity, but also the range of past environments that those deposits preserve. The New Zealand molluscan biodiversity curve is dominated by taxa that lived on the continental shelf, with only relatively low-diversity mollusc faunas from the deeper ocean. There are several possible reasons for this, both biological and related to fossil preservation. The key observation that Crampton *et al*. make is that sea-level rise can create a switch from predominantly shallow to deep marine deposits, and that this sampling bias may be the primary reason for the drop in species diversity seen at such times.

Concerns about how reliable a direct reading of the fossil record could be because of sampling bias were first raised in the 1970s (*4*). However, by 1981 most paleontologists believed that the fossil record—though imperfectly sampled—provided a reasonable representation of past diversity levels. As a result, many paleontologists in the 1980s and 1990s took the fossil record at face value to describe radiations, extinctions, and recovery periods in the geological past.

It will be interesting to see how many of these biodiversity patterns hold up to scrutiny. Alroy *et al.* have started to compile information on relative abundance to explore the effects of uneven collecting (*2*). Eventually, such studies will be able to tackle temporal bias in the environments that are preserved. However, there is unlikely to be a simple solution, as Crampton *et al.* point out, because tectonic setting is an important factor in determining how rock bias and sampled diversity are related.

Of course, a correlation between rock area and species diversity does not necessarily imply cause and effect. Both biodiversity and rock outcrop area could be driven by the same factor. Discriminating between high diversity because of more extensive outcrop and high diversity because of expanded areas of shallow marine seas will not be easy. As work on this question progresses, our view of marine diversity over time may come to be very different from the accepted view of the 1990s.

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NEUROSCIENCE

When Is a Word Not a Word?

Anthony R. McIntosh and Nancy J. Lobaugh

The human ability to use language is one of the most remarkable features of our species. Through speech and writing we communicate with astonishing complexity. Given this unique skill, we might expect that the human brain has developed certain areas that are specialized for language. Early studies of people with brain damage suggested an apparent division of labor between the brain's two hemispheres (lateralization), the left hemisphere being more important for language than the right (*1*). It is not clear which functions are lateralized to the right hemisphere, but they seem to involve visuospatial operations such as identifying the locations of objects in the environment. Although there is consensus on the general division of labor, the nature of the separation is not at all clear. Specifically, it is still a matter of debate whether lateralization depends on a linguistic stimulus or on the nature of the task (linguistic versus visuospatial) that the stimulus elicits. On page 384 of this issue, Stephan *et al*. (*2*) take a step toward resolving this conflict. They present neuroimaging evidence from human subjects suggesting that the functional split between the left and right hemispheres of the brain depends on what must be done with an incoming stimulus (the task), rather than the nature of the stimulus itself.

One difficulty in assessing the differential specialization of the two hemispheres is choosing the most appropriate stimulus. Thus, when assessing visuospatial judgment tasks, the tendency is to avoid a linguistic stimulus. Stephan *et al*. predicted that if lateralization depends on the task

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