

PALEONTOLOGY

Evolution of Animal Pollination

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The evolution of animal pollination in flowering plants (angiosperms) and the resulting coevolution and diversification of both angiosperms and major pollinator groups during the late Cretaceous (99.6 to 65.5 million years ago) is one of the classic stories of evolutionary biology (1). On page 840 of this issue, however, Ren *et al.* (2) challenge aspects of this story and hint at a much more complex ecological scenario for the evolution of plant-pollinator relationships.

An important feature of the traditional story is that the non-angiosperm seed plants living during the Mesozoic (251 to 65.5 million years ago) were mainly wind-pollinated. Although the fossil record of these plants shows evidence of possible animal pollination as early as the late Carboniferous (320 to 300 million years ago) (3), this evidence is open to interpretations of the size of pollen grains (apparently too large to be wind-dispersed), the possibly attractive function of reproductive organs, and patterns of damage by insects. The assumption is that although animal pollination may predate the evolution of the flowering plants, it was rare and unspecialized relative to what was to follow in the late Cretaceous (4).

Ren *et al.* now marshal evidence from an impressive range of sources—from comparative morphology of fossil insect mouthparts to elemental analysis of the fossils and their surrounding matrix—to propose that a previously overlooked group of Mesozoic scorpionflies was able to feed on a nectarlike fluid (5) produced by a group of now-extinct non-angiosperm seed plants. The authors suggest that the scorpionflies in turn pollinated the plants. This may be the earliest known example of coevolution between plants and pollinators. The evidence that Ren *et al.* present is compelling, and if they are correct, it will change our understanding of the early ecology and evolution of pollination by insects.

As Darwin (6) famously recognized when he speculated about the coevolution of flower and tongue length between the Madagascan orchid *Angraecum sesquipedale* and its (then unknown) moth pollinator, flowering plants have often evolved tubular structures that



Ancient legacy. Mesozoic scorpionflies (Mecoptera) probe the female reproductive organs of *Leptostrobus cancer*, a member of the extinct order Czekanowskiales. Modern scorpionflies are much less diverse than their Mesozoic antecedents. Although they only rarely visit flowers, this habit may be overlooked in modern species and could be a legacy of their distant ancestors.

hold nectar or protect reproductive organs. The plants can thus discriminate between flower visitors, enabling them to specialize on pollinators with appropriately sized mouthparts (7, 8). This match between mouthparts and flower depth (9) facilitates more accurate pollen placement, meaning that less pollen is wasted, and prevents nonpollinating animals from robbing nectar. It may be a major factor driving the diversification of some angiosperm genera (8) and structuring the patterns of interaction with pollinators in plant communities (10), but until Ren *et al.*'s study, it was considered unimportant in non-angiosperm pollination.

The 11 scorpionfly species described by Ren *et al.* have mouthparts that are both relatively long and consistent with fluid feeding by sucking. The species represent three different families, pointing to repeated convergent evolution of this feeding strategy, which in turn suggests that substantial quantities of nectarlike fluid (5) were available to these taxa. Ren *et al.* believe that the source was a group of non-angiosperm seed plants belonging to diverse, and mostly extinct, lineages.

Animals pollinated specialized seed plants even before flowering plants evolved.

All these species have reproductive organs that are poorly adapted to wind pollination (the previously presumed mode of reproduction for these taxa). Wind pollination requires that pollen-receptive areas are easily accessible to windborne pollen, which is clearly not the case for these plants. Pollen transfer by insects thus seems most likely, and the scorpionflies are the best candidates so far identified.

Some will find these claims controversial, particularly as a key piece of evidence is missing: The authors failed to find any pollen associated with these fossils. This is especially surprising for the amber-encased insects, where pollen preservation would be expected (11). Absence of evidence is not, however, evidence of absence, and further fossils may provide this information.

Biotic pollination was the dominant angiosperm pollination strategy by the late Cretaceous (12). Ren *et al.*'s research tests old notions that angiosperms evolved in a predominantly wind-pollinated world. Furthermore, it challenges us to rethink assumptions that early pollinators were short-tongued generalists that could only exploit open flowers with easily accessible nectar. Living representatives of the earliest diverging flowering plants have a diverse range of pollination systems (13), and many are far from generalized in their interactions with pollinators. The presence of long-tongued pollinating scorpionflies both before and at the same time as the first angiosperms allows us to imagine that flowering plants evolved deep flowers early in their radiation, coexisting with open, generalist flowers and gymnosperms as part of a specialist-generalist spectrum similar to modern plant communities (14).

Can modern assemblages of plants and pollinators be viewed as analogous to their Mesozoic counterparts, at least in terms of functionality, if not phylogenetic identity? Other Mesozoic insects have been suggested to be fluid-feeding pollinators (15, 16), and if this is so, then the scorpionflies described by

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Ren *et al.* were probably part of a larger fauna of insects visiting plant reproductive structures. The Mesozoic Era was biotically richer and more complex than previously realized. Studies such as that by Ren *et al.* provide a tantalizing glimpse of lost worlds of interactions between partners that are now extinct or considerably less diverse.

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CHEMISTRY

Capturing the Complexities of Molecule-Surface Interactions

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The simplest picture of a chemical reaction is that two molecules approach, climb a potential energy barrier as bonds get pulled apart in the transition state, and then separate, forming the new products. Molecules move in three dimensions and have internal motions such as vibrations, so a quantitative model requires molecules to move over a potential energy surface (1). Two reports in this issue address the added complexities that result when one of the reactants is a metal surface (see the figure). On page 829, Shenvi *et al.* (2) describe a method for the quantitative evaluation of one of the open questions in modeling these reactions: How is energy dissipated as the molecule approaches the metal surface? On page 832, Diaz *et al.* (3) present a pragmatic fix for the problem of calculating the potential energy surface that describes how molecular hydrogen (H_2) reacts with an atomically flat copper surface. Their approach allows almost every aspect of the experimental findings for this system to be reproduced.

For reactions between small molecules in the gas phase, potential energy surfaces calculated from first principles (without using inputs from experiments) have become quite successful in predicting product formation (4). However, for the more complex case of molecules interacting with a metal surface—which is of interest for understanding reactions in industrial catalysts—getting the calculations to agree with experiment is much more challenging, because the system to consider is extended and because energy dissipation to electronic excitations may become important (5).

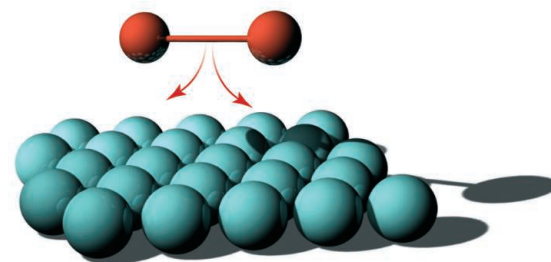
When molecules meet surfaces. The interaction of a molecule with a metal surface provides a challenge for the most sophisticated molecular structure calculations. Theory is rapidly moving toward a quantitative account of how molecules scatter off surfaces, as discussed by Shenvi *et al.*, or react and form bound surface species, as discussed by Diaz *et al.*

Modeling a chemical reaction is typically a two-step process. First, the interaction energy of the reactants is calculated for various geometric arrangements and then used to create the potential energy surface. The latter is then the basis for the calculation of the dynamics—that is, how the reactants will move and exchange energy until the products are formed. These analyses can be used to calculate reaction probabilities for real systems, where the molecules have a distribution of energies.

This two-step procedure rests on the thesis work of Robert Oppenheimer: the so-called Born-Oppenheimer approximation (BOA), which allows calculations of electronic energy independent of the motion (such as bond vibrations) of the much heavier nuclei (6). This approximation has been very successful for predicting molecular structures and reaction dynamics between molecules. However, the interaction with a metal surface is a particularly problematic case for applying the BOA because metals have a continuous electronic excitation spectrum, not discrete energy levels like single atoms and molecules.

It has been rigorously shown that the interaction of a molecule with a metal surface must dissipate energy into substrate electronic excitations; processes that dissipate energy in this way are called nonadiabatic (7–9). However, it is still not established how to predict the mag-

Two large computational studies describe how theory can better account for the way in which molecules scatter from or react with metal surfaces.



nitude of this energy, and the error introduced by the BOA, for a particular reaction system. The steadily increasing number of experimental studies that have reported evidence of nonadiabatic behavior emphasizes the need to understand the error created by the BOA [see (10) and references therein].

Shenvi *et al.* present a method that allows a quantitative account of nonadiabaticity and apply it to the particular case of a nitric oxide (NO) molecule scattering off a gold surface. They use data from a sophisticated experiment as a benchmark for their theoretical study. Wodtke and co-workers prepared NO molecules in a highly vibrationally excited state by means of laser techniques and observed that it loses vibrational energy several quanta at a time in the collision (11). Their experimental data are only consistent with a nonadiabatic coupling mechanism. An adiabatic model for this interaction would predict that the molecules scatter from a metal surface with the vibrational excitation intact, because the vibrational frequency is not in resonance with the vibrations of the surface atoms or the molecule-surface bond.

The vibrational motion of the NO molecule is connected with an oscillating shift in electronic energy for adding one more electron to the NO molecule. The vibrational motion is hence connected with an oscillat-

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