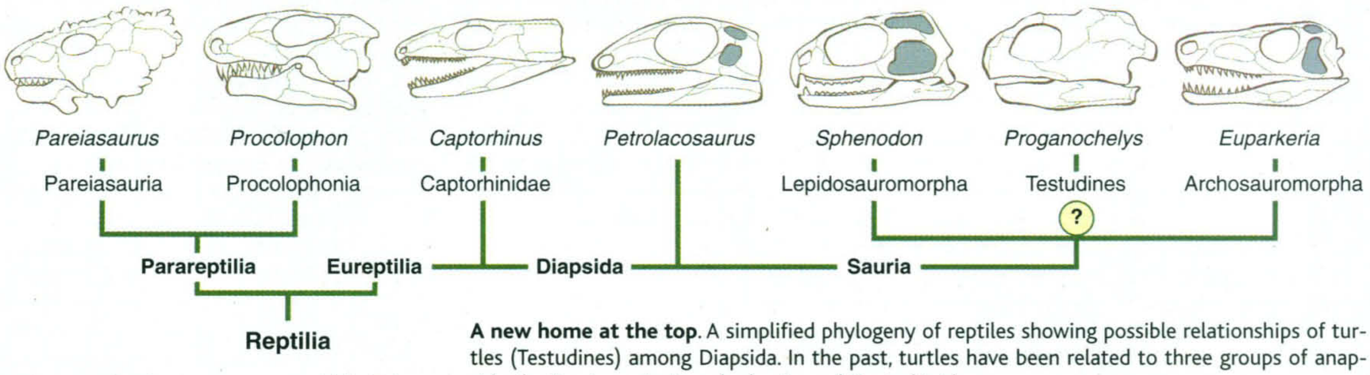
PERSPECTIVES: EVOLUTION

Turtle Origins

Olivier Rieppel

Textbooks portray turtles as the most primitive group of egg-laying animals (amniotes) in existence and extol their virtues as model organisms for primitive amniote organization and physiology. In their report published on page 998 of this issue, Hedges and Poling (*1*) present an exhaustive analysis of turtle relationships on the basis of DNA data. Their results, which support other recent analyses of protein (*2*) and DNA (*3*, *4*) sequences, indicate that instead of being related to the anapsid root of the reptile evolutionary tree, turtles nest in the tree crown, within Diapsida. These molecular data thus are partially congruent with morphological characters that also support diapsid (*5*), rather than anapsid (*6*), turtle relationships. However, the molecular data conflict with paleontological data as to where exactly turtles fit within diapsids. The DNA data also support a highly controversial relationship of the Tuatara, and it will be a challenge not only to paleontologists, as suggested by Hedges and Poling, but also to molecular systematists to resolve these conflicts.



A new home at the top. A simplified phylogeny of reptiles showing possible relationships of turtles (Testudines) among Diapsida. In the past, turtles have been related to three groups of anapsids, the Pareiasauria, Procolophonia, and Captorhinidae.

The older, Paleozoic reptiles have a skull in which the region behind the eye socket is completely covered by bone, the anapsid condition (see the figure). In the Diapsida two openings, the upper and lower temporal fossa, develop in the skull, presumably to facilitate muscle fiber attachment (see the figure). The skull of the earliest fossil turtle, *Proganochelys* from the Upper Triassic of Germany (*7*), shows a closed temporal region, suggesting that turtles are a surviving branch of Anapsida. Nevertheless, some details of bone configuration in the temporal region of the skull of *Proganochelys* and other turtles do not match the primitive pattern seen in Paleozoic reptiles (*5*), and a number of authors (*8*–*10*) have proposed that the anapsid turtle skull, where present, developed secondarily. The first comprehensive evaluation of turtle relationships (*11*) compared the bone and muscle characters of a broad range of extinct and living reptiles, and concluded that turtles are related to a herbivorous group of Paleozoic anapsids, the pareiasaurs. As the anapsid status of turtles became entrenched in textbooks, subsequent analyses of turtle relationships also found that they were related to these Paleozoic reptiles. Most recently, a pareiasaur relationship of turtles was supported by modern cladistic analysis (*6*).

But broadening the basis of anatomical comparison beyond the Paleozoic once again called into question the anapsid status of turtles (*5*), especially when Sauropterygia was included in the analysis. The Sauropterygia is a group of secondarily marine reptiles from the Mesozoic, commonly known as plesiosaurs and pliosaurs, which were adapted to a pelagic mode of life in the Jurassic and Cretaceous seas. Early representatives of the group from the Triassic lived in nearshore environments, and in many aspects of their anatomy resembled their terrestrial ancestors more closely than their later descendants. Recent reanalysis (*12*) of the data set (*5*) with Sauropterygia included increased support for the position of turtles within Diapsida, but also showed that it is the Sauropterygia that pulls the turtles up into the crown of the reptile tree.

The crown-group diapsids (Sauria) subdivide into two major evolutionary lineages, the archosauromorphs (crocodiles and birds and their fossil relatives such as dinosaurs) and lepidosauromorphs (the Tuatara, lizards, and snakes, and their fossil relatives). Morphological data (*5*, *12*) place the turtles as sister-group of the Sauropterygia, both nested at the base of the lepidosauromorph lineage. This contrasts with all available molecular data, which put turtles on the archosauromorph branch. Although the placement of turtles within Diapsida is the most parsimonious solution on the basis of all data at hand, the statistical support for both lepidosauromorph and archosauromorph affinities of turtles, on the basis of anatomical and molecular data, respectively, may be relatively weak in some cases. This reflects a high degree of independent evolution of morphological similarity (convergence) within anapsid and diapsid reptiles on the one hand, and the impact of a long separate evolution of the turtle branch on molecular characters on the other. However, an as yet unpublished morphological data set (*13*) places the Sauropterygia at the base of the archosauromorph lineage. The effect of inclusion of turtles into this data set has not yet been explored, but if Sauropterygia exert the same pull as they previously did (*5*, *11*), turtles might end up as archosauromorphs on the basis of morphological characters also.

Some authors have explored diapsid affinities of turtles among extant reptiles only and, by using anatomical and physiological characters, have placed them closer to crocodiles and birds than to the Tuatara (*Sphenodon*) and squamates (lizards and snakes) (*14*). Although there are some important similarities among turtles, crocodiles, and birds [such as the secondary subclavian artery (*15*)], the placement of the turtles on the archosauromorph lineage also raises important questions with respect to other characters that turtles share with the lepidosauromorph clade. One is the complex mesotarsal joint, which necessitates ontogenetic restructuring of the proximal tarsus in turtles, *Sphenodon*, and lizards (*7*,

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16). Yet, given the current support for diapsid affinities of turtles but the conflicting evidence for their position within diapsids, it is likely that future discussion will shift from whether turtles are diapsids, to where exactly they fit within the Diapsida. One conclusion can safely be reached: Turtles can no longer be blithely considered a model for primitive amniote organization and physiology.

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PERSPECTIVES: POLYMER SYNTHESIS

Making Polymers from Carbon Dioxide

Eric J. Beckman

Green plants accomplish the task of generating monomers and then polymers from CO_2 daily on a global scale. But what seems easy for plants remains a difficult problem for polymer scientists. To be fair, the situation in nature is quite different from that in a chemical factory. An industrial plant has a fixed capacity reflecting market need, and ideally all resources are used for the generation of a pure, bulk product. In contrast, the production capacity of living plants reflects the availability of raw resources and, thus, changes continuously. A mixture of products is produced to sustain the system. Polymer production rate, reactor size, raw material cost, and energy utilization in photosynthesis have thus evolved to fit the global ecosystem rather than the global marketplace. Nevertheless, nature has developed an efficient system for extracting an abundant raw material (CO_2) from dilute solution in the atmosphere and for generating a variety of monomers and subsequently polymers from it. Can we also find ways to make use of this inexpensive, relatively benign raw material to generate synthetic polymers? And will such synthesis routes lead to desirable, economically competitive products?

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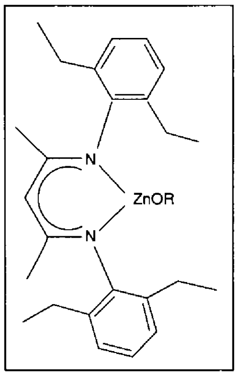
The use of CO_2 as a monomer in polymer synthesis is not new. Inoue and coworkers (*1*) reported copolymerization of CO_2 with an oxirane over a zinc catalyst in 1969. There is even earlier patent literature from the 1950s that claims the generation of polyureas from CO_2 and diamines under extreme conditions. Subsequent research, reviewed by Inoue in 1976 (*2*), Rokicki and Kuran in 1981 (*3*), and Super and Beckman in 1997 (*4*), has demonstrated that CO_2 can be copolymerized with a number of cyclic ethers, although the activity of the catalysts described was generally not high enough to warrant commercial interest. Industrial activity in the field accelerated in the 1980s, as evidenced by patent filings. However, these patents also reveal generally low catalyst activities, on the order of 50 grams of polymer per gram of metal (for comparison, activity can be well over 100,000 grams polymer per gram of metal for polyolefins). The products generated were not marketable, because of prohibitive production costs or undesirable physical properties. These results illustrate an important caveat for promoting the use of CO_2 as a raw material: Rates of reaction (at low catalyst loading) must be sufficient to support an industrial-scale process, and the materials generated must exhibit properties that provide a market advantage. Obviously, one could say this about any new synthetic polymer, and CO_2-based polymers are no exception.

In the 1990s, interest in the use of CO_2 as a raw material increased, quite possibly as a result of the mistaken notion that such technology could ultimately be used to reduce the atmospheric concentration of CO_2. Regardless of the initial motivation, increased industrial and academic research on the use of CO_2 as a raw material led to the discovery of new reactions of CO_2 with co-monomers, for example, with diynes, and to rapid improvements in catalyst activity in the copolymerization of CO_2 and cyclohexene oxide. Leading the way, Darensbourg and Holcamp developed a series of phenoxy zinc catalysts (*5*) that produce over 400 grams of polymer per gram of zinc, an order of magnitude improvement over previous catalysts. Soon afterward, Super *et al.* (*6*) developed a high-activity fluorinated (and thus soluble) zinc catalyst that was used to generate copolymers of CO_2 and cyclohexene oxide. In this approach, CO_2 was used as both monomer and solvent. Finally, in a recent paper (*7*), Coates and co-workers demonstrated the use of a zinc catalyst (see the figure below) that exhibits higher activity than any previous catalyst in the copolymerization of CO_2 and cyclohexene oxide. Importantly, this catalyst demonstrated high activity at low CO_2 pressure. Those familiar with the production of polyethylene will recall that the development of catalysts that rapidly generated polymer at low pressure improved the economics of production substantially. In fact, Cheng and co-workers used a catalyst design strategy resembling that used in the creation of metallocene catalysts for polyolefins, where the ligands are designed to allow insertion of the monomer at only a single well-defined site.



A superior catalyst. Catalyst developed by Cheng *et al.* (*7*) for the copolymerization of CO_2 and cyclohexene oxide. R may be a methyl or acetyl group.

Thus, over the past 5 years, we have seen orders of magnitude improvements in the activity of catalysts in the copolymerization of CO_2 and cyclohexene oxide. Where do we go from here? Although the recent studies (*5*–*7*) are impressive, a desperate need for their resulting product, poly(cyclohexene carbonate), has yet to materialize. This polymer exhibits a relatively high softening point of 135°C, but its overall physical properties, the current price of the cyclohexene oxide monomer, and other factors combine to prevent it from competing effectively in the restrictive world of commodity polymers. The recent work has

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