in Eq. 3, and OH radicals were presumably involved in the γ-ray–induced air oxidation of SO$_2$ in Eq. 6, the oxygen isotopy of secondary sulfate formation by photochemical processes is not necessarily exhaustively represented by the reactions that we have studied.

9. Samples were supplied by courtesy of R. N. Dietz, Brookhaven National Laboratory, Upton, N.Y.
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Juvenile-Adult Habitat Shift in Permian Fossil Reptiles and Amphibians

Abstract. *Among extant large reptiles, juveniles often occupy different habitats from those of adults or subadults and thus avoid competition with and predation from the older animals; small juveniles often choose cryptic habitats because they are vulnerable to a wide variety of predators. Evidence from fossil humeri and femora of Early Permian reptiles collected from sediments of several distinct habitats indicate that similar shifts in habitat occurred. Juvenile* Dimetrodon *seem to have favored cryptic habitats around swamp and swampy lake margins; adults favored open habitats on the floodplains. Similar patterns of habitat shift seem to be present in the reptile* Ophiacodon *and the amphibian* Eryops *and may have been common in fossil tetrapods of the Permian-Triassic.*

A shift in habitat from juvenile to adult is an important adaptation of living reptiles. Unlike the young of most birds and mammals, which enjoy parental protection until they are nearly adult in weight, most reptiles and amphibians act independently of their parents at hatching or shortly after, when the juveniles are a tiny fraction of the adult weight. Among living reptiles, crocodilians have the longest known period of parental care of young, up to 2 years, and yet the young become independent when they are only about 1/50 the weight of a sexually mature adult (*1*, *2*). Competition between successive age classes of one species of reptile can be severe, and subadults and adults may prey on juveniles (*3*). Small juveniles usually have more potential interspecific predators than adults and should prefer more hidden microhabitats. Subadult crocodilians have been observed to be partially segregated ecologically from adults (*1*, *2*); small juvenile crocodilians sometimes seem to prefer cryptic microhabitats, near shore swamps and reedbeds, and it has been suggested that young green turtles (*Chelonia mydas*) spend their first several years hidden within the floating *Sargassum* forests of the Caribbean (*4*). Because of their long independent ontogeny, one species of large reptile may fill the role of a dozen or more species of bird or mammal.

If the juvenile-adult habitat shift occurred among ancient reptiles and amphibians, recognition of this ontogenetic adaptation would be important in paleoecological reconstructions; otherwise ecological segregation by age in one species might be mistaken for the presence of two distinct species with different adult weights and habitat preferences. The record of ontogenetic habitat shift was studied in fossils from the Early Permian Red Beds of North Central Texas. The fauna of large amphibians and reptiles represents an early stage in the adaptive radiation of reptiles (*5*). The largest samples of single species occur in the Admiral and the overlying Belle Plains Formations. For 70 years, first Case and then Romer (*6*) collected thousands of specimens with good data on locality. Several habitats have been defined by sedimentological and paleontological characters. (i) The Geraldine Bonebed represents swamps choked with logs and other plant debris; sediments are mostly organic-rich clays with pyrite and other sulfides. Flat-bodied bottom-living amphibians which retained gills throughout their life are absent, indicating that the bottom water in this habitat was oxygen-poor, and the only common small aquatic amphibian is *Archeria*, an elongated eellike predator that could swim through a complex habitat of aquatic vegetation and terrestrial plant debris. (ii) The Briar Creek Bonebed represents swampy lakes; sediments are mostly dark mudstones with abundant siderite. Gill-breathing bottom-living amphibians are absent, and *Archeria* is common. (iii) The Rattlesnake Canyon localities represent lakes; sediments are mostly limy mudstones and limestones without plant debris. Gill-breathing amphibians (*Trimerorhachis*) are common, and *Archeria* is rare, suggesting that standing water was well oxygenated and relatively open and clear. (iv) West of William's Ranch represents mixed floodplain, small pond, and stream habitats; sediments are red-green mottled silty mudstones with soil carbonate nodules, lenses of fine dark mudstone, and small channel sandstones with basal mud-clast conglomerates and reworked soil carbonate nodules (*7*). Gill-breathing amphibians are locally common, and *Archeria* is relatively rare; small terrestrial amphibians with well-ossified, stout limbs are common (*8*).

The most commonly preserved elements that can be identified to genus are large limb bones, the humeri and femora. Good skulls are rare, and vertebrae, though numerous, were sometimes not collected. Romer, who recovered 90 percent of the fossils, collected every humerus and femur found in the field (*9*). The average sediment grain size in nearly all sites is in the clay-silt range, and the abundance of small limb bones suggests a low-energy environment with little hydraulic sorting of bones (*10*). All humeri and femora in the Case-Romer collections and in most other Early Permian collections from Texas were recently analyzed (*11*). *Dimetrodon*, a large finback predator, is the most common genus (*12*), and three species—large, medium, and small—are generally recognized. From the published records it appears that the small species preferred swamp and lake habitats, and the largest species preferred mixed floodplain, pond, and stream habitats (*13*). This pattern might in fact represent a shift in habitat of one or more species.

In the limb bones of most Early Permian reptiles and amphibians and extant lower tetrapods, the joint surfaces and the areas of muscle and ligament attachment became progressively better ossified during ontogeny. The fossil sample of the big flatheaded amphibian *Eryops* from the Briar Creek Bonebed shows the most striking case of ontogenetic ossification (Fig. 1A). The largest single sample of *Dimetrodon* bones, also from Briar Creek, is reported to contain bones of all three species. When the femora and humeri from Briar Creek were ordered by increasing size, the collection formed a rather smooth ossification sequence; the smallest size classes show the poorest surface ossification, and the largest size classes have completely ossified articular surfaces and rugosely ossified muscle attachment sites (Fig. 1B). Moreover, the collection showed a continuous allometric relation of femur breadth as a function of length (Fig. 1), and the variance within this allometric relation was no greater than that seen within a growth series of one species of large extant reptile (*14*). *Dimetrodon* specimens from

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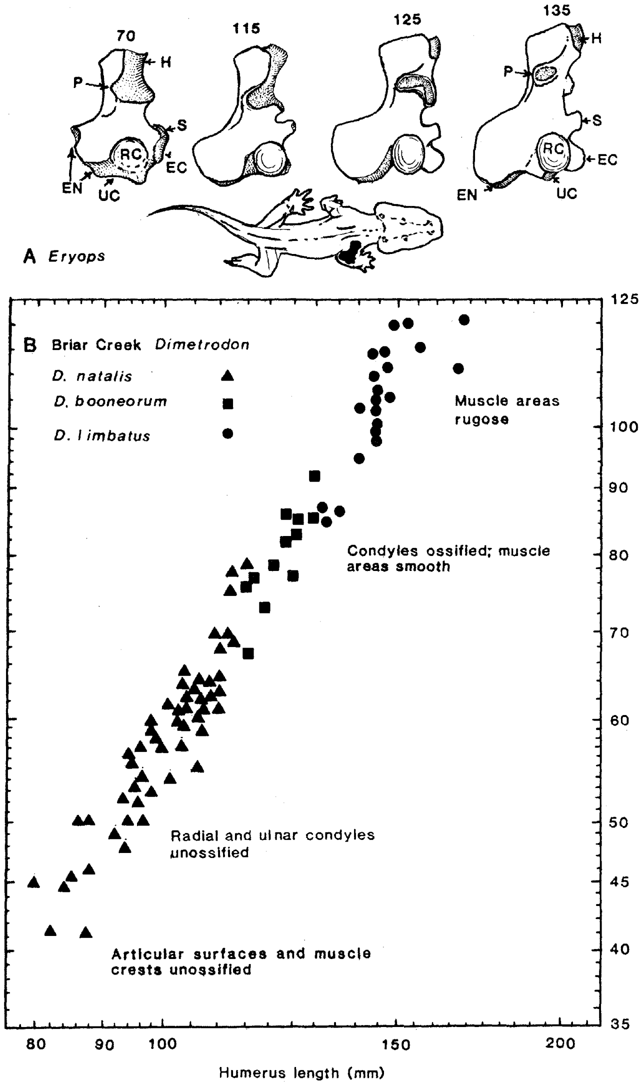

Fig. 1. (A) Progressive ossification with increasing size in the humerus of the big amphibian *Eryops*, from Briar Creek Bonebed. Humerus overall length given above the figures of the ventral view. Unossified areas stippled. *P*, pectoralis scar; *H*, head; *S*, supinator scar; *EC* ectepicondyle; *UC*, ulnar condyle; *EN*, entepicondyle; and *RC*, radial condyle. (B) Breadth as a function of length and ossification with increasing size in the *Dimetrodon* humeri from Briar Creek. Measurements of all the humeri identified in the literature (*13*) to species are shown.

the Admiral and Belle Plains Formations were then analyzed; with few exceptions the humeri and femora fell within the ossification sequence and the length-breadth allometric relation determined for the Briar Creek collection. These data suggest either that most of the *Dimetrodon* samples represent one species or, if there were more than one species, that they had similar limb proportions and the same adult size (*15*). In either case, differences in the size-frequency distribution of the bones among the habitats can be interpreted as the result of ontogenetic habitat choice (Fig. 2).

In the swamp locality, small juvenile *Dimetrodon* are the most common small vertebrate fossils, but there are no intermediate and large *Dimetrodon* (Fig. 2, Geraldine Bonebed) (*16, 17*). In the swampy lake locality, all size classes are present, but there is a marked peak in the distribution representing half-grown individuals (Fig. 2, Briar Creek). In the lake and mixed habitat localities the size classes are more evenly distributed, with fully adult animals making up a much larger part of the total collection than they do in the swamp and swampy lake localities (Fig. 2, Rattlesnake Canyon and West of William's Ranch). This pattern seems to represent ontogenetic habitat shift. The tangled vegetation in and around swamps was apparently used only by the youngest *Dimetrodon*; lake margins offered more open habitats and were preferred by subadults; adults favored open, well-drained floodplains and associated ponds and streams (*16*). The apparent shift from complex, cryptic habitats to more open habitats is similar to the pattern seen in extant crocodilians.

Distributions of the other large fossil tetrapods were also analyzed (*16*). *Ophiacodon* shows an apparent habitat shift, with juveniles relatively more common at the swampy lake site than at the lake site. Small *Eryops* juveniles are relatively more common in the swamp site than in the mixed habitat sites. Two big herbivores are present, *Diadectes* and the finbacked *Edaphosaurus*. *Edaphosaurus* is common only in the swamp site, where only fully ossified, apparently adult specimens occur; *Diadectes* is

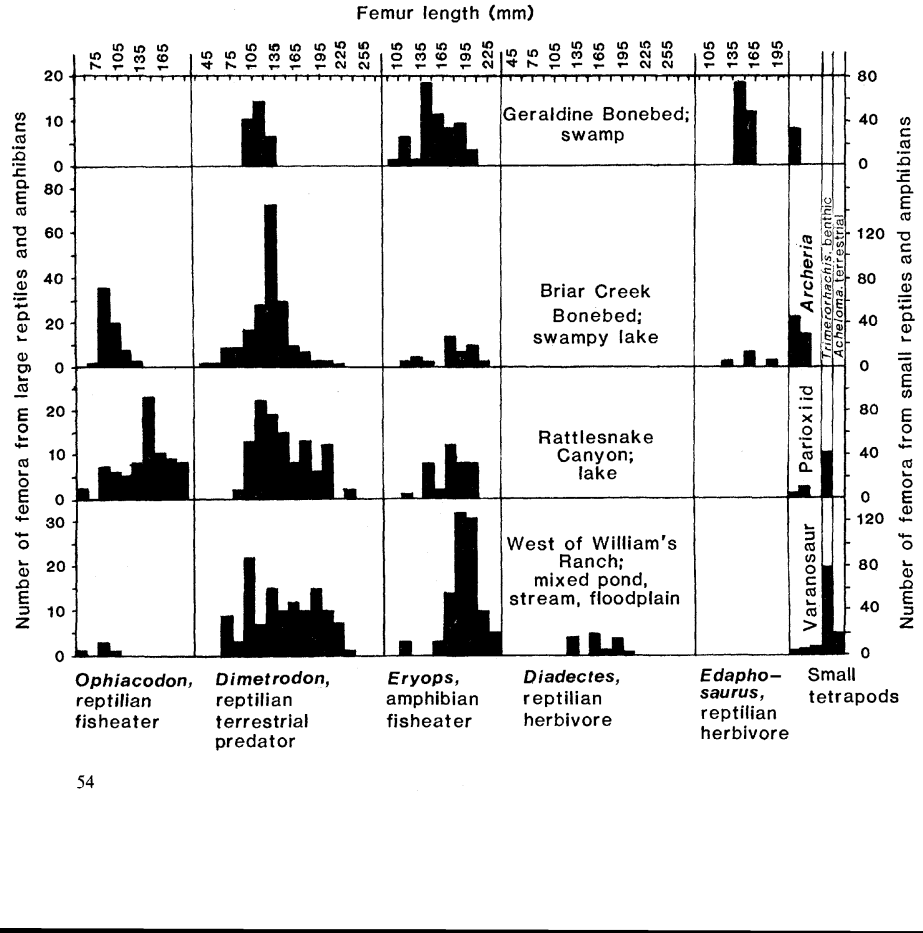

Fig. 2. Size-frequency distributions for the large reptiles and amphibians among the various habitats represented by the Admiral and Belle Plains Formations and the smaller tetrapods, which are divided into three categories: the swimmers which lacked gills as adults (*Archeria*, parioxiids, varanosaurs); the flattened, benthic forms which retained gills as adults (*Trimerorhachis*); and the stout-limbed, fully terrestrial types (*Acheloma*).

common only in the mixed-habitat sites, where both adults and subadults occur. The distribution of these herbivores supports Romer's suggestion, made 40 years ago, that *Edaphosaurus* preferred swamps (*18*). The preferred habitat of juvenile *Edaphosaurus* is not yet known.

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7. Sediments are described in the works cited by Case and Romer (*6*). Additional field studies and laboratory petrography was carried out by R.T.B. (unpublished observations). Red and green mottled mudstones with small carbonate nodules identical to those at William's Ranch are discussed by T. M. Bown [*Geol. Surv. Wyo. Mem. 2* (1979)], who argues persuasively that these structureless nodules grew in the B horizon of soils in floodplains that were at least seasonally well drained.
8. Geraldine Bonebed: American Tribune New Colony Subdiv., Sect. 98, Archer Co.; Briar Creek Bonebed: Dallas Co. School Land, Sect. 32, Archer Co.; Rattlesnake Canyon: Southern Pacific RR Survey A-412, Sect. 1, Archer Co.; and West of Williams' Ranch: J. Gibbs Survey A-566, Baylor Co. Maps of Romer's collection area are available in works cited in (*6*).
9. A. S. Romer, personal communication.
10. Some sediment samples from West of William's Ranch show small lenses of cross-bedded clay clasts and reworked carbonate nodules; cross sets were no larger than 7 cm.
11. All specimens in the following institutions were examined: Museum of Comparative Zoology, Harvard University; Yale Peabody Museum, Yale University; American Museum of Natural History, New York; Smithsonian Institution, Washington, D.C.; Field Museum of Natural History, Chicago; Museum of Paleontology, University of Michigan; Museum of Paleontology, University of Kansas; Paleontology Collection, University of Texas, Austin; Collections, Department of Paleontology, University of California, Berkeley; and Paleontology Collections, Biology Department, University of California, Los Angeles.
12. D. M. Bramble, *Paleobiology* **4**, 271 (1978).
13. A. S. Romer and L. Price, *Geol. Soc. Am. Spec. Pap. 28* (1940).
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15. Two *Dimetrodon* femora from the Upper Godwin Creek Bonebed, Belle Plains Formation, show complete ossification at 135 mm length, 50 mm less than for all other femora. These specimens are too slender to be *Secodontosaurus* (*13*) and indicate a small adult *Dimetrodon*-like genus.
16. Because most of the size-frequency distributions were not normal and because differences in the shape of the distributions among habitats for each species were of principal interest, the distributions were subjected to a χ^2 test for k independent variables [S. Siegel, *Nonparametric Statistics* (McGraw-Hill, New York, 1956), pp. 174–178]. The following sets of samples display significant departures from the hypothesis of a single common shape, at the .05 level: all *Ophiacodon*, $\chi^2(10) = 60$; all *Dimetrodon*, $\chi^2(15) = 39$; *Dimetrodon*, from West of William's Ranch and from Rattlesnake Canyon, $\chi^2(8) = 37$; *Dimetrodon*, from Geraldine Bonebed and Briar Creek, $\chi^2(6) = 35$; and all *Eryops*, $\chi^2(8) = 41$.
17. *Dimetrodon* had a dentition adapted for killing and dismembering relatively large prey. However, the genus probably did hunt semiaquatic reptiles and amphibians in the shallows and along stream and pond margins, as well as terrestrial species. Specimens of *Eryops* humeri at Harvard show deep teeth marks which match the cross-section shape of *Dimetrodon* teeth.
18. A. S. Romer, *Geol. Soc. Am. Bull.* **46**, 1597 (1935).
19. I thank the curators at the institutions enumerated in (*10*) for access to the collections; most especially, I am grateful to the late A. S. Romer for his interest in this project, though some of the results may be contrary to some of his conclusions; when shown the ossification sequence for Briar Creek, Romer commented that ". . . yep, all those *natalis* could be juveniles."

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Carbon Functionalities in Amber

Abstract. *High-resolution nuclear magnetic resonance spectra of the carbon nuclei in powdered amber, obtained by using the techniques of magic angle spinning and cross polarization, provide detailed information about the types of carbon functionalities. The entire spectrum of Baltic amber (succinite) is identical for several samples. Baltic amber shows minor differences from Sicilian amber and drastic differences from Burmese, Romanian, and Bohemian ambers.*

Because of its use over several millennia as a raw material for decorative objects and its origin from ancient plant materials, amber has been of interest to the archeologist (*1*) and the paleobotanist (*2*) alike. Knowledge of the chemical structure of amber would be of use both in associating a given object with its geographic origin and in determining the botanical identity of the tree from which the source resin of amber came. Efforts to obtain a detailed description of the chemical structure of amber have been thwarted by its noncrystallinity and poor solubility. Thus are eliminated the two most general structural tools, x-ray crystallography and solution phase nuclear magnetic resonance (NMR) spectroscopy (*3*). Infrared spectroscopy of powdered amber has provided the most useful structural information to date and has been particularly successful as a diagnostic for Baltic amber (succinite) (*4*). The analytical problems with amber are very similar to those with coal. Both materials have a complex organic structure and are poorly soluble in spectroscopic solvents. Recently developed methods for obtaining high-resolution NMR spectra of solids (*5*) have been exploited very successfully in the analysis of coal and related materials (*6*). Consequently, we examined a variety of ambers by this technique, and we report here a detailed description of the chemical types of carbon present.

Figure 1 shows a typical spectrum of the ^{13}C resonances of a powdered sample (0.5 g) of Baltic amber, taken with magic angle spinning and cross polarization (CPMAS) and averaged over multiple scans (*7*). Three other Baltic samples of various colors and opacities had essentially identical spectra. Whereas the infrared spectrum was diagnostically useful primarily in the C–O stretching region (1250 to 1100 cm^{-1}), the ^{13}C spectrum is diagnostic over the entire range of resonances. Compared to analogous spectra of coal, those of amber have remarkable fine structure. Either amber contains fewer free electrons that would broaden the resonances, or coal contains a much wider distribution of functional groups that would lead to an almost featureless pattern.

Because the amber spectra contain considerable fine structure, a relatively detailed description of the carbon functionalities is possible. The resonances from approximately 0 to 100 ppm are due to saturated carbons and comprise about 86 percent of the total for the Baltic ambers. Those from 100 to 160 ppm are due to unsaturated carbons (alkenic and aromatic) and comprise 11 percent of the total. For comparison, the saturated:unsaturated ratio for coal is about 50:50. Finally, the resonances above 160 ppm in frequency are from carbonyl groups and comprise 3 percent of the total. Integrated intensities in CPMAS spectra include uncertainties due to the differing efficiencies of polarization transfer from the proton pool to the various carbon nuclei. In addition, for heterogeneous samples such as coal, wood, or amber the protons may have different relaxation times in different regions of the sample. The integrations should be valid, however, for detecting and comparing trends among related samples, as in the present study. The chemical shifts are reliable to 1 ppm.

The carbonyl resonances in Fig. 1 are entirely from acids and their derivatives. There are no aldehydes or ketones, which would resonate above 190 ppm. The relative amounts of esters (CO_2R), acids (CO_2H), and (probably) ionized acids (CO_2^-) are represented by the distinct peaks respectively at 173, 180, and 187 ppm. It is clear that most of the acid functions are present as esters. Succinic

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