cluding ions trapped in  $C_{60}$  (18) and shipin-a-bottle synthesis of ions trapped in zeolites (19), the distinctive materials produced with our method are monolayer, room-temperature matrices that hold molecularly dispersed polyatomic cations. The implications for spectroscopy are apparent. The placement of isolated ions a few angstroms from a metal should give rise to interesting spectroscopic effects associated with the mixing of the discrete molecular orbitals of the matrix-isolated ions and the diffuse bands of the metal. The potential for preparing surfaces and interfaces with unusual electronic and magnetic properties is also evident. The extraordinary selectivity offered by the availability of a wide variety of projectile ions should allow the production of longlived metastable structures of various types at self-assembled monolayer surfaces.

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- Beam sizes were estimated using a highly focused 15-keV beam of Ga<sup>+</sup> after modification of two F-SAM surfaces at 10 eV (area 50 mm<sup>2</sup>) and 60 eV (area 3 mm<sup>2</sup>).
- 14. The number of sputtered ions was estimated by converting the total analog-to-digital converter counts in the sputtered ion decay curve of the deposited species into an ion current and estimating corrections for the gain, transmission, and spot sizes of the experiment.

- 15. The high-resolution TOF-SIMS analysis was performed with a TFS series instrument (Charles Evans & Associates, Redwood City, CA) with 15-keV Ga<sup>+</sup> ion sputtering. The TOF-SIMS data were taken about 36 hours after the surface sample was modified with  $C_3H_{10}Si_2O^{35}Cl^+$  (m/z 153) and  $C_3H_{10}Si_2O^{37}Cl^+$  (m/z155) from projectile ions  $C_8H_4Si_2O^{36}Cl^+$  (m/z 181) and  $C_5H_{14}Si_2O^{37}Cl^+$  (m/z 153) and  $C_3H_{10}Si_2O^{37}Cl^+$ (m/z 155) had about equal intensities as determined by in situ 60-eV  $^{132}Xe^+$  sputtering analysis before the sample was sent to 3M Center (St. Paul, MN) for TOF-SIMS analysis.
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- 17. These experiments were performed with a Finnigan

TSQ 700 triple-quadrupole mass spectrometer with the ion source filament turned off. The sample was mounted on a specially constructed direct insertion probe that heated the surface from room temperature to 400°C in 40 s. Well-defined peaks from desorbed ions were observed in plots of ion abundance versus time. The trapped ions that are thermally released might not be as tightly held as those desorbed by ion impact.

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## Gliding Mechanism in the Late Permian Reptile Coelurosauravus

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A complete skeleton of the oldest known flying reptile, *Coelurosauravus jaekeli*, from the Upper Permian of Germany, and reexamination of other specimens demonstrate that this animal had a gliding apparatus unlike that of any other tetrapod. The lateral gliding membrane was supported by radially disposed, greatly elongated bony rods of dermal origin in the thoracolumbar region, rather than by internal skeletal elements such as ribs and limb bones. The rods are independent of the ribcage and arranged in distinct bundles to form a cambered wing.

Extant and fossil terrestrial vertebrates have developed a diversity of gliding mechanisms (1, 2): (i) flattening of the body by drawing in the ventral surface of the body (the flying snake, Chrysopelea); (ii) spreading of webbed feet or membranous flaps along the hind edges of the limbs, in some instances accompanied by flattening of the body (some flying frogs such as Hyla miliaria and Rhacophorus *rheinwardtii*); (iii) expansion of a lateral skin fold between the fore- and hindlimbs [flying phalangers (Marsupialia), flying lemurs (Dermoptera), and flying squirrels]; (iv) expansion of a lateral membrane supported by elongated, flexible thoracolumbar ribs [as in the gliding lizard *Draco* (3)]; and (v), as (iv), but with elongated, rigid ribs, which form hinge-joints with the considerably enlarged transverse processes of the dorsal vertebrae [Late Triassic Kuehneosauridae (4, 5)]. Although many birds, especially large forms, are skilled gliders, bats rarely glide, perhaps

because they cannot control gliding and vary wing area as much as birds can (2). Here we describe a new skeleton of the oldest known flying tetrapod, *Coelurosauravus* (6, 7), and show that it had a different gliding mechanism from those examples mentioned above.

The Late Permian Coelurosauravus is a small diapsid reptile most closely related to the Neodiapsida, the clade including all archosaurian and lepidosaurian reptiles (8). The most diagnostic features of Coelurosauravus are the chameleon-like frill at the back of the skull roof, formed primarily by the squamosals, and the presence of numerous long, rodlike bones that supported a lateral gliding membrane (8, 9). These rods were originally misinterpreted as the fin rays of a coelacanth fish superimposed on a small reptilian skeleton and were, for the most part, removed during preparation of the holotype of Coelurosauravus jaekeli (10). When correctly recognized as genuine parts of the skeleton in other specimens, they were first interpreted as greatly elongated ribs (11) and later as the long distal segments of bipartite ribs (8). However, the supposed proximal rib elements (8) are short and strongly curved, much like the dorsal ribs in most other small reptiles. This feature is especially evident in an excellent-

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**Fig. 1.** Coelurosauravus jaekeli, SMNK 2882 PAL, nearly complete skeleton. Note the numerous long rods for support of a lateral gliding membrane and the very long tail. Image width, ~23 cm.

ly preserved partial skeleton from the Marl Slate of Eppleton Quarry (northeast England) (8, 9). The curvature of these ribs would rule out distal articulation with the rodlike elements. Furthermore, the inferred one-to-one correspondence between proximal ribs and distal rods would result in an improbably long thoracolumbar region comprising 24 to 28 vertebrae (8, 12).

An almost complete skeleton of C. jaekeli (Fig. 1) has only 13 thoracolumbar vertebrae but at least 22 rods on each side. This fossil demonstrates that, contrary to previous reports (8), the Eppleton specimen with 12 dorsal vertebrae, and a partial skeleton from the Kupferschiefer of Bodental, Hesse, with 13 (8, 12, 13), both preserve most or all of the thoracolumbar region. The anterior seven rods in the new specimen form a distinct bundle. A second bundle consists of five, a third of four, a fourth of three, and a fifth of two rods. The posterior six or seven rods appear to be single rods. Corresponding bundles with identical numbers of rods are preserved in the Eppleton skeleton and in a specimen from the Kupferschiefer of Bauhaus, Hesse (13). The arrangement of the bundles in the fossils indicates that the wing segments could be folded over each other when the wing was brought back against the body. In life, the configuration of bundles would have produced an anteroposteriorly curved (cambered) gliding membrane, which was ideally suited to its function as an airfoil.

Expansion of a lateral gliding membrane supported by rods is only possible when the rods are arranged in a more or less radial fashion. The Eppleton specimen shows that the anterior rods had a radial disposition, and, along with the Ellrich skeleton, demonstrates that the first bundle includes the longest rods supporting the wing. The rods in the more posterior bundles become progressively shorter (Fig. 2). If the right wing of the Eppleton fossil represents a relaxed, almost unfolded position of this structure, the leading edge of the wing of Coelurosauravus was oriented at an angle of about 45° to the long axis of the body. The trailing edge is marked by the distal ends of the more posterior rods. The long, flexible tail of Coelurosauravus (Fig. 2) may have aided in stabilization and steering during flight, much as in extant Draco and gliding mammals (9).

We interpret the elongated rods in *Coelu*rosauravus as neomorphic dermal ossifications that formed the internal support of a lateral gliding membrane. Our scanning electron microscopy (SEM) investigation of samples removed from the new skeleton reveals that the rods are hollow and have thin walls with external sculpturing composed of fine longitudinal grooves and ridges. The gliding mechanism did not involve the thoracolumbar ribcage (12). The forelimbs were also not integrated into the membrane but may have aided in steering during gliding flight.

Coelurosauravus predates the next oldest known reptilian gliders, the Late Triassic Kuehneosauridae (4, 5), by at least 20 million years. Unlike in other tetrapods, the lateral gliding membrane in Coelurosauravus was entirely supported by independent, rodlike dermal mineralizations, rather than by internal skeletal elements.



**Fig. 2.** Outline reconstruction of *C. jaekeli* in dorsal view, with the left wing folded against the body and the right wing fully spread. Body proportions are based on SMNK 2882 PAL (with a reconstructed snout-vent length of 18 cm). Details of individual bundles of rods were reconstructed on the basis of that fossil and the Eppleton specimen. The distal portions of the larger rods are shown as curved backward as a result of tension produced by the intervening gliding membrane when the wing is spread. The exact number and disposition of the small, delicate rods near the posterior margin of the wing is uncertain.

Gliding could be used to facilitate escape from predators and for energy-efficient foraging in terrain with varied topography (14). Present-day gekkonid lizards provide an excellent structural model for the development of a lateral gliding membrane. The parachuting membrane of the flying gecko *Ptychozoon* developed from a lateral skin fold on the body (14). As in *Coelurosauravus*, it does not involve the limbs or ribcage.

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cific absorption edge of the element of in-

terest, in this case Sr. Excitation and back-

scattering of Sr K-edge electrons provide

information about the local environment

(out to several nearest-neighbor shells) of

the Sr atoms, at Sr concentrations as low as

1000 parts per million (ppm).

## Strontianite in Coral Skeletal Aragonite

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An x-ray spectroscopic study of scleractinian coral skeletons indicated that, although some strontium substitutes for calcium in the aragonite structure, at concentrations of about 7500 parts per million, as much as 40 percent of the strontium resides in strontianite (SrCO<sub>3</sub>). A doublet peak in the Fourier transform of the extended x-ray absorption fine structure of the coral corresponded to six metal and 13 oxygen neighbors surrounding strontium at about 4.05 angstroms in strontium-substituted aragonite and at about 4.21 angstroms in strontianite. Thus, the mechanism of the temperature-sensitive partitioning of strontium between seawater and coral skeleton used for paleothermometry is unexpectedly complex.

Strontium/calcium ratios in scleractinian corals have been used to reconstruct past sea surface temperatures (SSTs) on the basis of the observed temperature dependence of Sr partitioning between seawater and coral skeleton (1). However, in some cases SSTs derived from Sr/Ca ratios differ from those derived by other techniques (for example, oxygen isotopes), and the origins of these differences are not clear (2). Because  $SrCO_3$  is isomorphous (3) and shows at least partial solid solution with aragonite (4), it generally has been thought (4, 5)that Sr substitutes for Ca in biogenic and inorganic marine aragonites, although there is recent evidence to the contrary (6).

To characterize the site of Sr in aragonite scleractinian corals, we used x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectroscopy. In these experiments, an intense, monochromatic beam of x-rays, usually from a synchrotron source, is tuned gradually across the energy of a spe-

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collected live, one collected live and then bleached, and one collected dead; all had  $\sim$ 7000 ppm of Sr), three Acropora palmata (AP) corals (one of Pleistocene age and two collected live; all had ~7500 ppm of Sr), and an aragonitic pelecypod bivalve (with  $\sim$ 1500 ppm of Sr) (7). We used calcite, inorganic aragonite, SrCO<sub>3</sub>, SrO, and SrO<sub>2</sub> as standards for structural comparison and extraction of EXAFS phase shifts and scattering amplitudes. Measurements were conducted at the Stanford Synchrotron Radiation Laboratory (SSRL) using XAS techniques (8).

We analyzed four Montastrea annularis

(MA) corals (one of Holocene age, one

The aragonite and calcite XANES (Fig. 1) were taken at the Ca K-edge (4038.5 eV), whereas the other spectra were taken at the Sr K-edge (16104.6 eV). In calcite, Ca and Sr are distinguished from the other structural sites by a distinctive doublet at the top of the absorption rise for calcite and Sr in calcite. Fourier transforms of the  $K^3$ -weighted EXAFS data (from  ${\sim}3.5$  to 12  ${\rm \AA}^{-1}$ ) at the K-edges corresponding to the XANES, along with the appropriate phase shift (Ca-O or Sr-O), yielded peaks close to the expected crystallographic distances (Table 1). The measured metal-metal distances are also close to the reference distances established by x-ray diffraction (XRD) (9).

The Sr K-edge XANES of the different coral species and ages appear identical at the resolution presented in Fig. 2. The absence of the doublet at the top of absorption rise indicates that Sr is not in the calcite form of CaCO<sub>3</sub>. The XANES features resemble Sr in SrCO<sub>3</sub>, SrO<sub>2</sub>, and SrO, and to a lesser extent, Ca in aragonite (Fig. 1).

Table 1. Summary of Fourier transforms, XRD, and least-squares fits to EXAFS data. N<sub>1</sub>, coordination number (±20%) from least-squares fit;  $R_{\rm f}$ , bond length (±0.05 Å) from least-squares fit;  $\Delta\sigma^2$ , meansquared relative displacement (with respect to SrO standard) from least-squares fit; Eo, inner potential (treated as arbitrary parameter) from least-squares fit; SD, standard deviation of least-squares fit to data; R., bond length from peak of Fourier transform; XRD, x-ray diffraction data for coordination number and bond length; Sr, strontium in aragonite sample; MA, M. annularis coral; AP, A. palmata coral; PEL, pelecypod bivalve; H, Holocene age; P, Pleistocene age; I, collected live; d, collected dead; b, bleached. Calcite (rhombohedral) and aragonite (orthorhombic) are polymorphs of CaCO<sub>3</sub>; SrCO<sub>3</sub> is isomorphous with aragonite.

Sample	N <sub>f</sub>	R <sub>f</sub> (Å)	$\Delta\sigma^2$ (Ų)	E <sub>o</sub> (eV)	SD	R <sub>t</sub> (Å)	XRD (Å)
Calcite Aragonite SrO Strontianite Sr (MA I) Sr (MA I, b) Sr (MA d) Sr (MA H) Sr (AP I-14) Sr (AP I-15) Sr (AP P) Sr (PEL)	10.6 9.0 8.8 8.6 9.3 8.8 8.8 8.8 8.9 8.9 9.6	2.57 2.59 2.55 2.56 2.56 2.56 2.56 2.56 2.55 2.55	0.0030 0.0006 -0.0004 -0.0002 -0.0008 -0.0007 -0.0003 -0.0004 0.0007	1.17 0.44 0.00 0.17 0.56 1.01 0.29 0.30 -0.31 0.14	0.187 0.189 0.225 0.274 0.202 0.273 0.294 0.286 0.284 0.253	2.36 2.53 2.58 2.57 2.64 2.57 2.57 2.57 2.60 2.57 2.57 2.50 2.52	VI-2.36 IX-2.53 VI-2.58 X-2.61 IX-2.64