tions, that is, they are associated with the removal of a 60° wedge from the hexagonal network (*12, 16, 17*). On the other hand, graphite deforms by "kinking" when it is under compressive stresses parallel to the basal planes. In general, the growth-induced stresses seem to be sufficiently large to activate this mode of plastic deformation, as shown in some of the illustrated tubules in (*11*). However, part of the compressive stresses may also be relieved by the formation of heptagons associated with −60° disclinations, that is, with the insertion of a 60° wedge that causes negative curvature (hyperbolic points). The occurrence of pentagon-heptagon pairs minimizes the long-range stresses. These considerations may readily be extended to helices. They explain why most of the graphite helices show deformation patterns, which are characteristic of kinking, preferentially along the inner rim (*11*), or polygonization suggestive of the presence of (5-7) ring pairs as discussed in (*10*).

The mobility of a particle promoting tip growth is appreciable, because the particle rests on a film of carbon atoms that has fluid-like characteristics (*3*). If the spatial hodograph of the particle is asymmetric with respect to the line cd (Fig. 6A), the continuity condition cannot be satisfied. The planar hodograph is then asymmetrical as well. More material tends to be deposited on one side of the symmetry line cd than on the other side. This difference causes the particle to be tilted about the line cd, thereby changing the azimuth of the line connecting the minimum and maximum in the spatial hodograph. Tilting of the particle may thus lead to a change in azimuth of the hodograph, which in turn changes the bending axis of the tubular surface. One can thus envisage that under rather special conditions the particle describes a precession motion, imposing a continuous rotation in the azimuth of the hodograph. This rotation would lead to the formation of a coiled tube wound on a toroidal surface rather than on a cylinder. An example of a tubule that was presumably formed partly in this manner is shown in Fig. 1D.

Because the catalytic activity of a particle may change in the course of time due to local poisoning, for example, the hodograph is often time-dependent. The resulting tubular surfaces may then have complicated shapes such as a helix with a variable pitch. However, the radius of the tubule remains roughly constant because this parameter depends mainly on the size of the active particle. The growth-induced stresses may further lead to complicated deformation patterns of the tubules that may in part account for the observed polygonization of helices (*10, 11*). The stresses could be periodically relieved by the introduction of (5-7) ring pairs when the elastic limit is exceeded.

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4 April 1994; accepted 6 June 1994

A Devonian Tetrapod from North America

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An early tetrapod fossil from the Upper Devonian of Pennsylvania (Catskill Formation) extends the temporal range of tetrapods in North America and suggests that they attained a virtually global equatorial distribution by the end of the Devonian. Derived features of the shoulder girdle indicate that appendicular mechanisms of support and propulsion were well developed even in the earliest phases of tetrapod history. The specialized morphology of the pectoral skeleton implies that the diversity of early tetrapods was great and is suggestive of innovative locomotor patterns in the first tetrapods.

The origin of terrestrial vertebrates is one of the major events in the history of animal life. The transition from life in water to life on land was extremely complex. Current controversy centers on the evolutionary relations between fish and tetrapods, the timing of tetrapod origins, the early biogeographic history of tetrapods, and the functional and physiological changes that allowed the invasion of terrestrial ecosystems (*1, 2*). Fossil evidence of the earliest tetrapods comes from a small number of widely scattered Upper Devonian localities [~370 to 362 million years ago (Ma)]. The most complete material consists of partially articulated skeletons of *Ichthyostega* and *Acanthostega* from East Greenland (*3*). Less completely preserved remains of other Upper Devonian tetrapods have been recovered from sites in Scotland (*4*), Latvia (*5*), Russia (*6*), and Australia (*7*). Devonian tetrapod trackways, which are much less reliable evidence, have been reported from Australia (*8*) and Brazil (*9*). Here we describe an Upper Devonian tetrapod from continental North America. The specimens include early, well-preserved shoulder girdles that provide an understanding of forelimb function during the early diversification of tetrapods.

Hynerpeton bassetti gen. nov. sp. nov. (*10*) was collected in 1993 near the village of Hyner in Clinton County, Pennsylvania, USA. The specimens (*11*) are from the Duncannon Member (*12*) of the Catskill Formation. They are Middle to Upper Famennian in age (Late Devonian, ~365 to 363 Ma).

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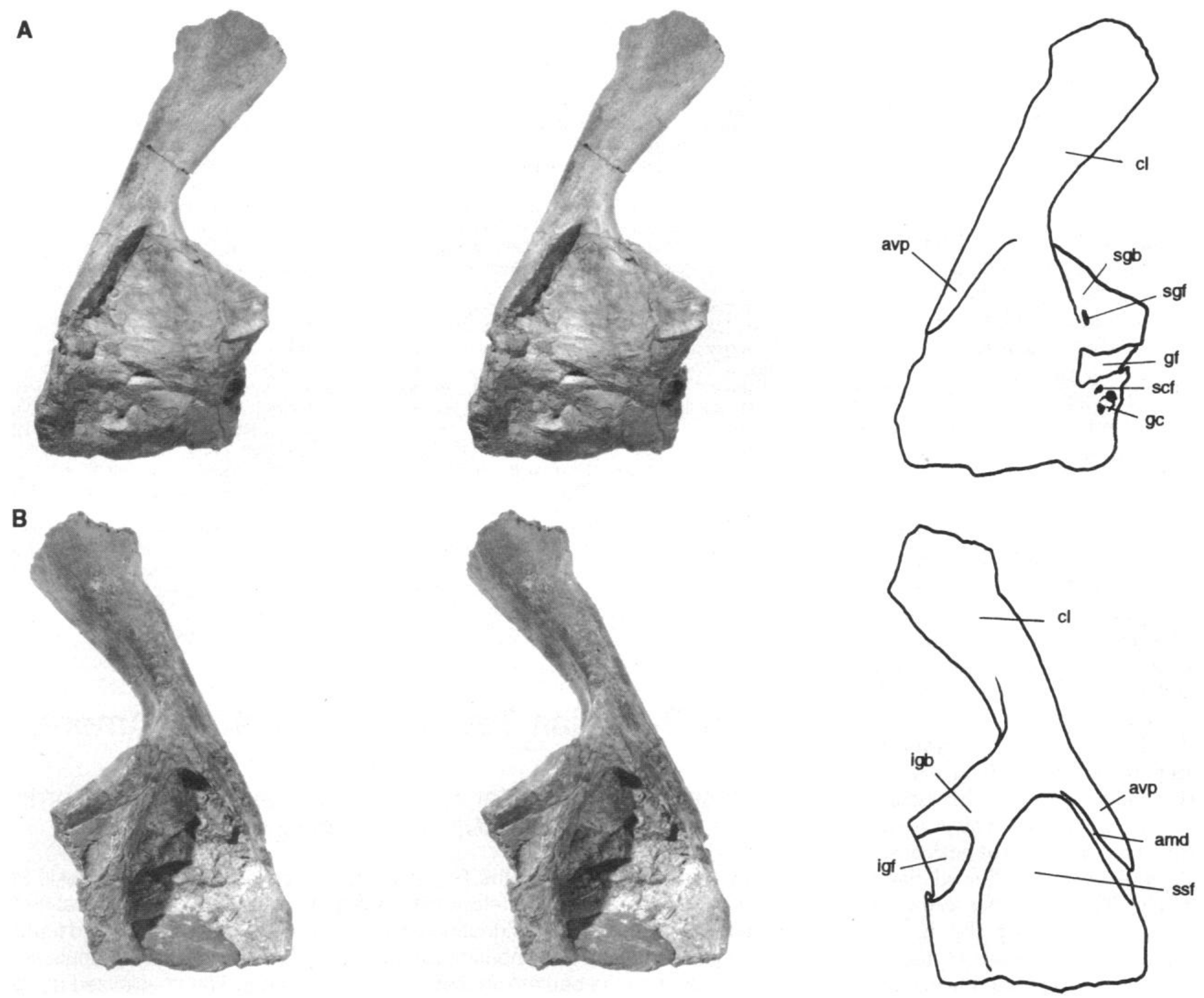

Fig. 1. ANSP 20053, holotype of *H. bassetti*. Stereopairs of the left cleithrum and scapulocoracoid. (**A**) Lateral view, (**B**) medial view. Abbreviations: cl, cleithrum; avp, anteroventral process; amd, anteromedial depression; sgb, supraglenoid buttress; igb, infraglenoid buttress; igf, infraglenoid fossa; sgf, supraglenoid foramen; scf, supracoracoid foramen; gc, glenoid canal; ssf, subscapular fossa; gf, glenoid fossa. Specimen height, 7.8 cm.

This species is diagnosed by a unique combination of primitive, derived, and autapomorphic features (Figs. 1 and 2). The primitive characters shared with other Devonian tetrapods are an unornamented cleithrum fused ventrally to the scapulocoracoid, an enlarged scapulocoracoid that makes up the bulk of the shoulder girdle, a coracoid region that is eggshell-thin ventrally, a robust supraglenoid buttress, a glenoid fossa that faces posterolaterally, and a prominent anteromedial depression. The derived tetrapod features (shared with the Russian Devonian tetrapod *Tulerpeton*) are the lack of a postbranchial lamina, dorsal expansion of the cleithrum, and anterior recurvature of the cleithrum (*13*). The autapomorphic features of *H. bassetti* are a deep subscapular fossa (open ventrally) that extends the entire length of the scapulocoracoid, extensive development of muscle scars on the dorsal border of the subscapular fossa, a massive infraglenoid buttress that composes the entire posteromedial portion of the scapulocoracoid, and the presence of an infraglenoid fossa (*14*).

The discovery of *H. bassetti* extends the known geographic range of early tetrapods and indicates that they had a virtually global equatorial distribution by the end of the Devonian (Fig. 3). This extensive early distribution suggests that tetrapods either arose during the Early Devonian and dispersed when the continents were closely associated or arose later in the Devonian and dispersed using marine routes (*15, 16*).

H. bassetti was found in fine-grained, nonmarine floodplain deposits of the Catskill Formation. This formation was deposited along a northeast-trending shoreline at about 20°S (*17*). The environmental setting was a broad coastal plain crossed by numerous northwestward-flowing fluvial systems that merged into a muddy shoreline of extensive delta plains (*18*). Sedimentary rocks at the tetrapod locality are green- and red-colored sandstone to mudstone in fining-upward cycles 5 to 10 meters thick, which are indicative of meandering stream systems. *H. bassetti* occurs in association with an abundant assortment of fish, including the large rhizodontid "rhipidistian" *Hyneria lindae*, two species of undescribed osteolepiformes, undescribed paleoniscoid fish, at least one species of the acanthodian *Gyracanthus*, and at least one species of the antiarch placoderm *Bothriolepis*. The fossil material recovered at the site is undistorted, occasionally articulated, and locally abundant.

H. bassetti was recovered at least 50 m below the Catskill Formation's contact with the overlying Huntley Mountain Formation (*19*). Paleobotanical evidence indicates that the Devonian-Mississippian boundary lies within the lower half of the Huntley Mountain Formation (*20*). This stratigraphic position suggests that *H. bassetti* is Middle to Upper Famennian in age (~365 to 363 Ma), which is older than *Ichthyostega*, *Acanthostega*, and *Tulerpeton*, which are uppermost Famennian (*21, 6*). *H. bas-*

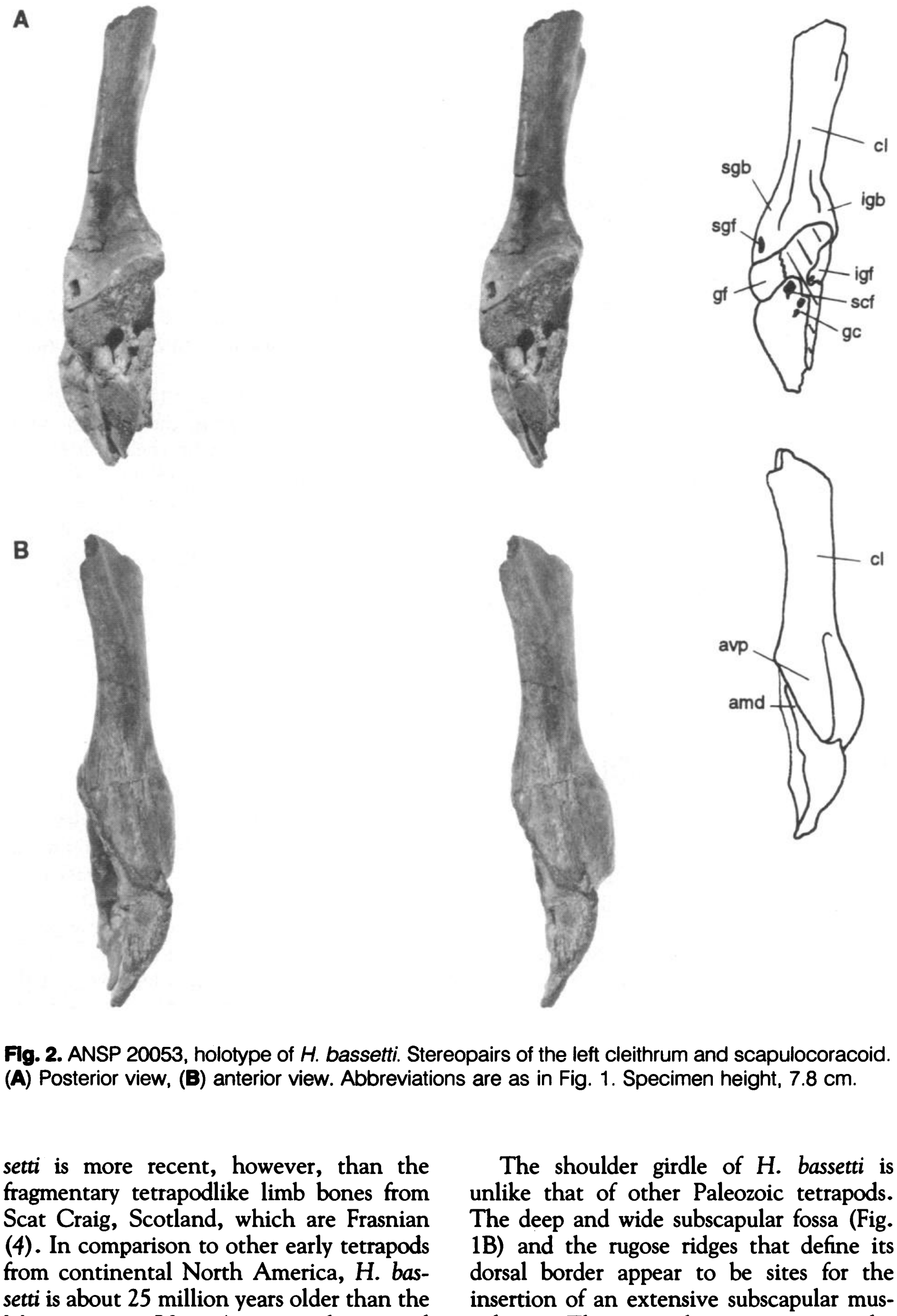

Fig. 2. ANSP 20053, holotype of *H. bassetti.* Stereopairs of the left cleithrum and scapulocoracoid. (**A**) Posterior view, (**B**) anterior view. Abbreviations are as in Fig. 1. Specimen height, 7.8 cm.

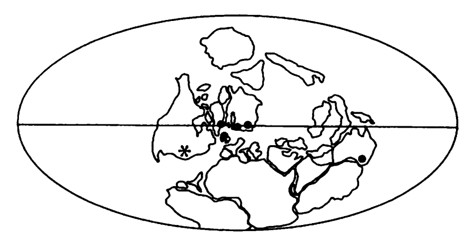

Fig. 3. Map of paleocontinental positions in the Upper Famennian (*17*) showing the location of Upper Devonian sites that have produced tetrapod skeletal material. Asterisk marks the location of the North American discovery.

setti is more recent, however, than the fragmentary tetrapodlike limb bones from Scat Craig, Scotland, which are Frasnian (*4*). In comparison to other early tetrapods from continental North America, *H. bassetti* is about 25 million years older than the Mississippian (Visean) tetrapod material from Iowa (*22*) and about 10 million years older than the tetrapod material reported from the Early Mississippian (Tournaisian) of Nova Scotia (*23*).

H. bassetti has numerous derived features; some are unique, whereas others are shared with later forms. The postbranchial lamina, which is found on the anterior border of the cleithrum in *Ichthyostega, Acanthostega*, and gill-breathing bony fish, defines the posterior margin of the opercular chamber for internal gills (*24*). *H. bassetti* is derived in the loss of this feature (Fig. 2B), which indicates that at least one tetrapod lineage had lost internal gills as early as the Middle to Upper Famennian.

The shoulder girdle of *H. bassetti* is unlike that of other Paleozoic tetrapods. The deep and wide subscapular fossa (Fig. 1B) and the rugose ridges that define its dorsal border appear to be sites for the insertion of an extensive subscapular musculature. These muscles act as a muscular sling that connects a mobile shoulder girdle to the axial skeleton. This broad and prominent area for insertion indicates that the muscles for pectoral support and mobility were more developed in *H. bassetti* than in other known Devonian tetrapods.

The morphology of the shoulder girdle of *H. bassetti* also suggests that it was capable of powerful protraction, retraction, and elevation of the forelimb. The size and position of the infraglenoid fossa (Fig. 1B) indicate that large limb retractor muscles originated on the posteromedial side of the scapulocoracoid and inserted on the proximal humerus. The rugose posterolateral margin of the anteroventral process (Fig. 1A) defines the anterior edge of a broad shallow fossa for the origin and course of muscles directed posteroventrally to elevate and protract the limb. The areas for attachment of these muscles are well developed and suggest that forelimb protraction and retraction were major components of support and locomotion in *H. bassetti.*

Devonian tetrapods show a mosaic of terrestrial and aquatic adaptations; many structures, such as limbs, may have served dual purposes (*25*). *H. bassetti* is derived in characters of the respiratory and locomotor systems, which underwent major changes during the invasion of land by vertebrates. The loss of internal gills in *H. bassetti* is suggestive of an early shift from opercular mechanisms of respiration to a more derived tetrapod pattern. The forelimb of *H. bassetti* has two major functional features: an extensive muscular connection between the axial skeleton and the pectoral girdle, and well-developed protractors, retractors, and elevators of the forelimb. This confirms the hypothesis that appendicular mechanisms of propulsion and support were at a premium in the earliest phases of tetrapod evolution (*15, 26*). The emphasis on girdle and forelimb support and mobility can be interpreted as adaptive in aquatic and terrestrial environments.

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11. The specimen shown in Figs. 1 and 2 is a holotype, Academy of Natural Sciences of Philadelphia (ANSP) number 20053, a virtually complete left scapulocoracoid and cleithrum. The articular surface of the glenoid fossa is incomplete posteromedially. The specimen is relatively undistorted and is preserved in three dimensions. A referred specimen, ANSP 20054, is another left cleithrum. It includes a complete dorsal blade but lacks regions ventral to the base of the anteroventral process. The lateral surface of the blade is exposed. This specimen is also undistorted.
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16 March 1994; accepted 31 May 1994

Fullerenes in the 1.85-Billion-Year-Old Sudbury Impact Structure

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Fullerenes (C_{60} and C_{70}) have been identified by laser desorption, laser desorption post-ionization, and high-resolution electron-impact mass spectrometry in shock-produced breccias (Onaping Formation) of the Sudbury impact structure in Ontario, Canada. The C_{60} isotope is present at a level of a few parts per million. The fullerenes were likely synthesized within the impact plume from the carbon contained in the bolide. The oxidation of the fullerenes during the 1.85 billion years of exposure was apparently prevented by the presence of sulfur in the form of sulfide-silicate complexes associated with the fullerenes.

The discovery and synthesis of fullerenes (*1*), and their unusual stability against photodissociation and thermal degradation (*2*), soon led to the hypothesis that fullerenes may be ubiquitous and abundant in the universe, particularly in the outflows of carbon stars (*3*). Fullerene molecules (*4*), or perhaps their hydrogenated counterparts (fulleranes) (*5*), have been suggested as carriers of visible diffuse interstellar bands, although so far spectroscopic searches for fullerenes and fulleranes in space have led to negative results. Fullerenes have been reported in impact residues in a small crater on NASA's Long Duration Exposure Facility (*6*). Several studies have investigated fullerenes in meteorites (*7*), but so far none have been detected (*8*). On the Earth, natural fullerenes have been identified in fulgurite (*9*), a glassy rock that forms where lightning hits the ground, and shungite (*10*), a highly metamorphosed carbon-rich rock within Precambrian sediments. Preliminary results also suggest that trace quantities of fullerenes may be present in sedimentary deposits associated with the Cretaceous-Tertiary impact event (*11*), possibly produced during global conflagnation. Based on these reported terrestrial occurrences, it would appear that fullerenes are not a ubiquitous form of carbon on Earth.

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Because fullerenes form under highly energetic conditions and at intense temperatures and pressures, we decided to investigate meteorite impact deposits on Earth for the presence of natural fullerenes. We report here the discovery of fullerenes (C_{60} and C_{70}) in a unit of shock-produced impact breccias (Onaping Formation) from the Sudbury impact structure in Ontario, Canada. The fullerenes were identified in separate samples by laser desorption and laser desorption post-ionization time-of-flight (TOF) methods and by high-resolution electron-impact mass spectrometry (EIMS).

The Sudbury structure (*12*) is an elliptical basin 60 km long and 27 km wide, elongated in an east-northeast direction. Ore deposits occur around the margins of the basin and in radial dykes emplaced into older rock. The outer margin of the basin is outlined by the Sudbury Nickel Irruptive, an igneous body that directly overlies deposits of copper-nickel sulfides. To the north and west, the structure is underlain by older Archean granitic and migmatitic rocks of the Superior Province, while to the south and east the rocks are predominately Proterozoic metasedimentary and metavolcanic rocks of the Huronian Supergroup and felsic plutonic rocks of similar age (*12*). Samarium-neodymium isotopic data on whole rocks and minerals and uranium-lead studies of zircons within the Sudbury complex indicate a formation age of ~1850 million years ago (Ma) (*13*). The proposal that the Sudbury structure was produced by a large meteorite impact is supported by the identification of shatter cones (distinctive conical fractures that are extensively developed in the target rocks), a variety of shock-induced petrographic features in basement rocks and in the overlying Onaping Formation (*14–16*), and by comparison with other structures in which an impact origin is either proven or strongly suggested (*17, 18*).

The Onaping Formation is an 1800-m-thick unit interpreted as allochthonous breccia formed during the impact event and redeposited in the resulting crater (*14–16*), but it differs from the ejecta at other impact craters in being highly carbonaceous (total organic carbon of ~0.5 to 1.0%), especially in the upper parts of the formation. The source of the carbon has long been (and still is) a mystery. In addition to being enriched in carbon, the Onaping Formation contains numerous fragments of devitrified glasses and shocked rocks. There is also evidence for sulfide enrichment from the melting of crustal rocks by the impact event to produce the Sudbury magmas that generated the ores in the lower part of the structure (*19*).

We examined three samples of the carbon-rich upper unit, the so-called "Black Tuff." The samples were collected from