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Author(s): Paul F. Hoffman
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Did the Breakout of Laurentia Turn Gondwanaland Inside-Out?

PAUL F. HOFFMAN

Comparative geology suggests that the continents adjacent to northern, western, southern, and eastern Laurentia in the Late Proterozoic were Siberia, Australia-Antarctica, southern Africa, and Amazonia-Baltica, respectively. Late Proterozoic fragmentation of the supercontinent centered on Laurentia would then have been followed by rapid fan-like collapse of the (present) southern continents and eventual consolidation of East and West Gondwanaland. In this scenario, a pole of rotation near the Weddell Sea would explain the observed dominance of wrench tectonics in (present) east-west trending Pan-African mobile belts and subduction-accretion tectonics in north-south trending belts. In the process of fragmentation, rifts originating in the interior of the Late Proterozoic supercontinent became the external margins of Paleozoic Gondwanaland; exterior margins of the Late Proterozoic supercontinent became landlocked within the interior of Gondwanaland.

THE INTERVAL ENCOMPASSING THE Vendian to Cambrian transition [0.7 to 0.5 billion years ago (Ga)] is perhaps the most enduring enigma in historical geology. The advent and subsequent evolutionary explosion of metazoa were accompanied by extreme fluctuations in sea level, global climate, and the isotopic and chemical compositions of seawater (*1–3*). That these changes are related to the fragmentation of a Late Proterozoic supercontinent (*4*) is an idea that stemmed from the observation that rifting and continental breakup occurred contemporaneously around the margins of Laurentia (North America and Greenland), Baltica (Baltic shield and Russian platform), Siberia, and parts of Gondwanaland (*5–7*). However, the relation of the hypothetical supercontinent to the continents forming Gondwanaland (South America, Africa, Arabia, India, Antarctica, and Australia) is unresolved because reliable paleomagnetic data for the interval are sparse. In most reconstructions of the Late Proterozoic supercontinent, Gondwanaland is treated as a coherent entity (*1, 6, 8–11*), despite evidence that its consolidation was broadly contemporaneous with fragmentation of the northern continents (*12, 13*). Not surprisingly, some question the reality of a supercontinent that may have disintegrated before it had formed. In the absence of sea-floor magnetic anomalies, pre-Mesozoic continental reconstructions are necessarily speculative. However, correlation of Precambrian orogenic belts that were once continuous but are now truncated at modern or ancient continental margins provides a means of establishing former linkages between separated continents. On the basis of such evidence, I present a qualitative but testable model for the breakup of a Late Proterozoic supercontinent centered on Laurentia and the subsequent assembly of Paleozoic Gondwanaland.

Northeastern Siberia (all directions refer to present-day coordinates) has been proposed as the conjugate margin to southwestern Laurentia in the Late Proterozoic on geological (*14*) and paleomagnetic (*15*) grounds. The evidence is permissive but not conclusive. U-Pb zircon geochronology indicates that the Anabar and western Aldan shields (Fig. 1A) of Siberia consist of crust that formed before 3.0 Ga and underwent high-grade metamorphism and anatexis at 2.8 to 2.6 Ga and again at 2.0 to 1.9 Ga (*16*). In Laurentia, only the Thelon-Taltson magmatic zone (Fig. 1A) in northwest Canada has such a history (*17*), but this zone is truncated beneath the plains of east-central Alberta and does not appear to reach the Cordillera (*18*). However, the zone does extend northward where it is truncated by the Paleozoic Franklin orogen in the Arctic (*17*). Thus, if the Anabar and Thelon-Taltson belts were originally connected, Siberia was most likely conjugate to the Arctic (*19*) margin of Laurentia (Fig. 1A).

Jefferson (*20*) proposed that western Laurentia was flanked in the Late Proterozoic by the eastern margin of the Australian craton together with the margin of the East Antarctic craton corresponding to the Transantarctic Mountains (Fig. 1A). This proposal stemmed from comparative Late Proterozoic stratigraphy of the respective Australian and Laurentian margins (*20*). Recently, Moores (*21*) and Dalziel (*22*) have bolstered the restoration and fixed its position by pointing out that a tectonic boundary equivalent to the Grenville orogenic front of west Texas reappears in Antarctica near the east coast of the Weddell Sea (Fig. 1A). Moores (*21*) suggested that the Grenvillian (1.3 to 1.0 Ga) belt loops back around the East Antarctic craton (by way of the Eastern Ghats of India) into the Albany-Fraser belt (Fig. 1A) of southwest Australia (*23*). The reconstruction implies that the northwest corner of Laurentia lay adjacent to north-central Australia in the Late Proterozoic. There are indeed remarkable parallels in Early Proterozoic geology and U-Pb geochronology between the Wopmay orogen in northwest Canada and the Mount Isa, Pine Creek, Tennant Creek, and Halls Creek inliers of northern Australia (Fig. 1A). The main orogenic event in each area occurred from 1.90 to 1.88 Ga—the Calderian orogeny in Canada (*24*) and the Barramundi orogeny in Australia (*25*). Each area experienced intense, mainly felsic volcanism and plutonism from 1.88 to 1.84 Ga (*26, 27*), and the felsic magmas were derived from crustal sources having Nd model ages of 2.4 to 2.0 Ga (*28, 29*). The comparison not only supports the proposed reconstruction (*20–22*) but also implies that northwest Laurentia, east Antarctica, and the Australian craton were fellow travelers from 1.9 until 0.6 Ga (*30*).

If East Gondwanaland (India-Australia-Antarctica) separated from western Laurentia, then which continent or continents lay adjacent to eastern and southern Laurentia before the opening of the Iapetus Ocean? Earlier works have advocated northwest Africa (*8*), western South America (*6*), Arabia (*7, 15*), and Baltica (*31*). Pre-Grenvillian tectonic zones provide piercing points that pin Baltica adjacent to northwest Britain (*31*), which was then a part of Laurentia off southeast Greenland (Fig. 1A). To the south, the Appalachian and Ouachita margins of Laurentia are confined to the Grenville orogen. Therefore, cratons that are bordered by Grenvillian belts are more likely to have been conjugate to southeastern and

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Continental Geoscience Division, Geological Survey of Canada, Ottawa, Ontario, K1A 0E8.

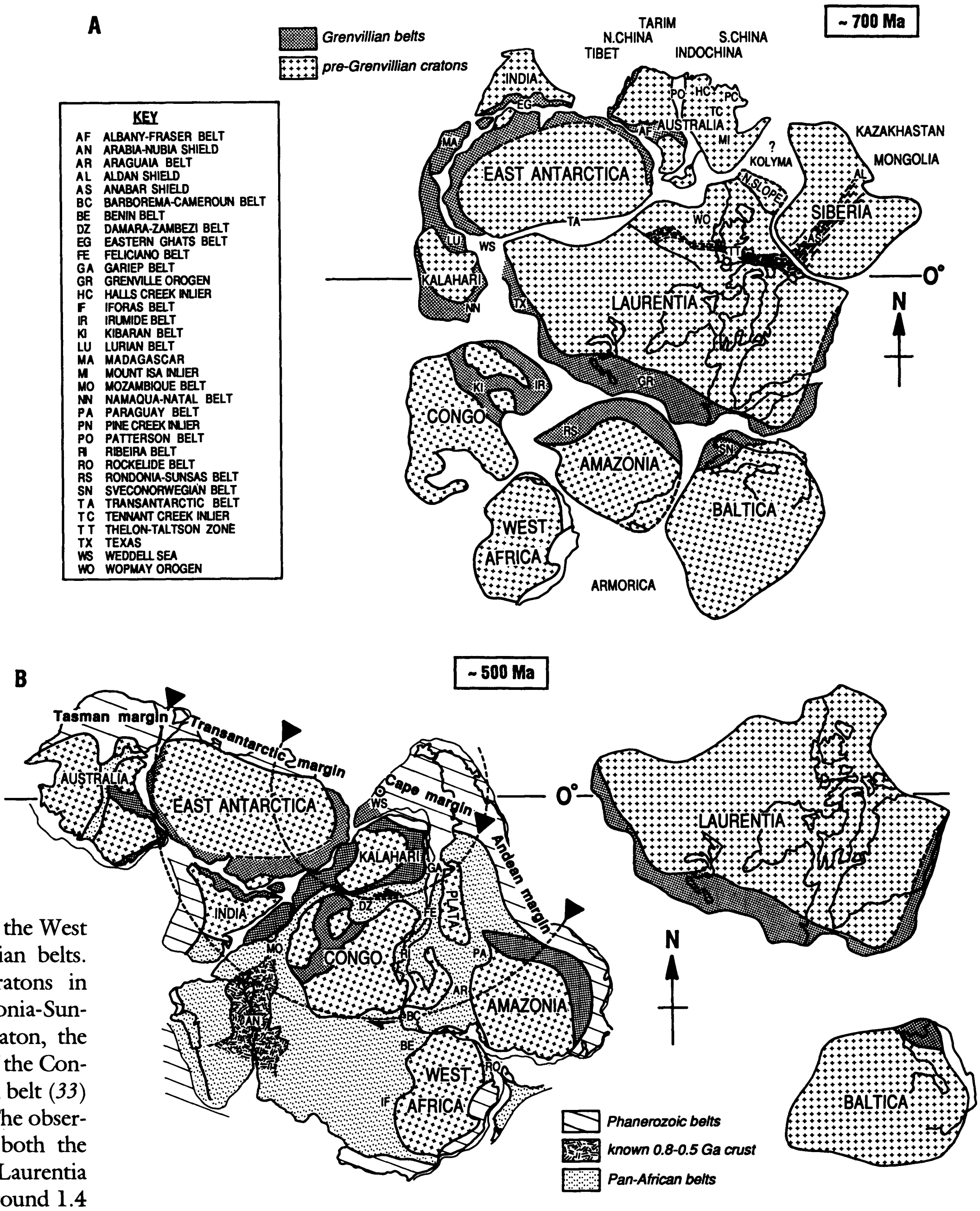

Fig. 1. (**A**) Reconstruction of the proposed Late Proterozoic supercontinent. Restoration of Baltica is from Gower (*31*), Amazonia from (*6*), and Australia-Antarctica from (*21*) and (*22*). The loose fit of the Congo, Kalahari, West Africa, and Amazonia cratons reflects changes in their size and shape as a result of tectonic shortening during the subsequent assembly of Gondwanaland (Pan-African orogeny). (**B**) Late Cambrian paleogeography after the breakout of Laurentia (*56*), abandonment of Baltica (*57*), and ensuing amalgamation of Gondwanaland (*56*). Dashed lines are small circles around a pole of rotation in the Weddell Sea.

southern Laurentia than those like the West African craton that lack Grenvillian belts. Grenvillian belts marginal to cratons in Gondwanaland include the Rondonia-Sunsas belt (*32*) of the Amazonia craton, the Irumide and Kibaride belts (*13*) of the Congo craton, and the Namaqua-Natal belt (*33*) of the Kalahari craton (Fig. 1A). The observation that Grenvillian rocks in both the Namaqua-Natal belt and southern Laurentia have Nd model ages that cluster around 1.4 Ga (*34, 35*) lends further credence to the proposed reconstruction (Fig. 1A), in which they are in close proximity. Other than Baltica, none of the Eurasian cratons is known to have a marginal Grenvillian belt. Late Proterozoic juxtaposition of Arabia and Laurentia is unlikely: Arabia is composed of Late Proterozoic orogenic belts containing much juvenile crust (*36*). The only equivalent belts in Laurentia (the Avalonian terranes of the Appalachians) did not arrive there until 0.4 to 0.3 Ga (*37*). Therefore, the cratons most likely to have been conjugate to eastern and southern Laurentia in the Late Proterozoic are Baltica, Amazonia, Congo, and Kalahari (Fig. 1A).

The separation of Australia-Antarctica and Amazonia-Baltica from western and eastern Laurentia, respectively, implies that Gondwanaland was assembled through a fan-like collapse of its constituent cratons. Collapse could have been achieved by counter-clockwise rotation of Antarctica-Australia and dextral translation (with or without clockwise rotation) of Amazonia, relative to Laurentia (Baltica is left behind) (Fig. 1B). Available paleomagnetic data are compatible with the implied rotation (*10, 11, 22*) and with large-scale convergence between East and West Gondwanaland, possibly lasting until the Late Cambrian (*12*). Rotation about a pole near the Weddell Sea would account for the dominant transcurrent motion observed in east to east-northeast trending belts of Pan-African (0.8 to 0.5 Ga) age. Such belts would have approximated small circles of rotation. In the Borborema-Cameroun belt (Fig. 1B), there is geological (*38, 39*) and paleomagnetic (*40*) evidence for dextral shear. For the Damara-Zambezi belt (Fig. 1B), there is geological evidence for dominantly transcurrent shear (*41*) and paleomagnetic evidence for a 35° clockwise rotation of the Kaapvaal craton with respect to the Congo craton (*33, 42*). For orthogonal Pan-African belts, like the Mozambique belt (Fig. 1B) that welds East and West Gondwanaland, a pole of rotation near the Weddell Sea would account for the observed dominance of thrusting (*38, 41, 43*), the northward increase in the width of crust produced by subduction-accretion tectonics (*36, 44*), and the southward increase in metamorphic grade and basement reactivation (*44, 45*). The southern limit of the Mozambique belt is uncertain. Some workers have envisaged that the Late Proterozoic collision zone extends between the Kalahari and East Antarctic cratons (*44*). Others have interpreted the southernmost Mozambique belt as essentially Grenvillian (Lurian) in age (*46*): this relation implies that the Kalahari craton belongs to East Gondwanaland and that the collision zone between East and West Gondwanaland is transformed from the Mozambique belt to the Gariep belt by way of the Damara-Zambezi belt (Fig. 1B). Accordingly, the Damara-Zambezi belt should have experienced net dextral (*33*) rather than sinistral (*41*) transcurrent shear.

The proposed reassembly turned the constituent cratons of Gondwanaland inside-out: the external Paleozoic margins of Gondwanaland (the Tasman, Transantarctic, Cape, and Andean margins of Fig. 1B) originated as rift zones in the interior of the Late Proterozoic supercontinent. Conversely, the external margins of the Late Proterozoic supercontinent, some of which had been consuming plate boundaries since before 0.7 Ga, became landlocked within the interior of Gondwanaland. Such margins border the Mozambique (*44*), Arabia-Nubia (*36, 47*), Benin-Iforas (*38, 48*), Gariep-Feliciano-Ribeira (*49*), and Paraguay-Araguaia-Rockelide (*38, 50, 51*) mobile belts (Fig. 1B).

Obviously, it is impossible for Australia-Antarctica to have been connected to western Laurentia and Amazonia to have been simultaneously connected to eastern Laurentia if Gondwanaland was already a coherent entity. Thus, the final assembly of Gondwanaland must postdate the breakout of Laurentia for the scenario proposed here to be viable. This requirement constitutes a clear test of the model. Rifting had begun in western Laurentia by 0.78 Ga (*17*) and in eastern Laurentia by 0.60 Ga (*52*). A minimum age for continental breakup of 0.62 to 0.56 Ga is inferred from the onset of long-lived thermal subsidence along both margins (*6*) and stratigraphic evidence suggests an Early Cambrian rift-to-drift transition (*53*). However, the Cordillera and Appalachians contain no equivalents of the Late Proterozoic Beardmore (*54*) and Pampean (*50*) orogenies that affected the Transantarctic and Andean margins, respectively. This observation implies, if these orogenies are correctly dated, that East and West Gondwanaland had separated from Laurentia before the end of the Proterozoic. The age of consolidation of East and West Gondwanaland is also uncertain. Subduction of oceanic lithosphere in the Arabian-Nubian shield ended at 0.64 to 0.62 Ga (*36, 47*). To the southeast, however, a terminal collision of latest Cambrian age (0.51 to 0.50 Ga) has been postulated between an active margin in northeast Somalia and East Gondwanaland (*44*). It may be significant that the seawater $^{87}Sr/^{86}Sr$ curve reaches a peak of 0.7096 in the Middle Cambrian that is the highest value in the last billion years (*3*). Evidently, the Middle Cambrian was a time of extremely rapid erosion of old radiogenic crust. The erosion must be a consequence of tectonic uplift, as it cannot be accounted for by glaciation (no continental glaciations of Cambrian age) or eustasy (global sea level rose during Cambrian time). In the absence of major contemporaneous orogeny outside of Gondwanaland, the seawater $^{87}Sr/^{86}Sr$ curve suggests that mountain building associated with the collision of East and West Gondwanaland culminated in the Middle Cambrian.

Thus, the proposed scenario may or may not be viable, depending on which set of age estimates is confirmed. As some events in the critical interval are dated isotopically and others biostratigraphically, accurate chronometric calibration of fossil zones is all important. Recent evidence that the base of the Cambrian might be in the age range 0.54 to 0.52 Ga (*55*), in contrast to earlier estimates of 0.59 to 0.57 Ga, highlights this problem. Regardless, it seems safe to conclude that if my scenario is valid, fragmentation of the Late Proterozoic supercontinent and the ensuing amalgamation of Gondwanaland must have occurred rapidly. The contemporaneous crises in the biotic, oceanic, and climatic realms may have occurred in response to such an abrupt tectonic reorganization.

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Conjugated Polymer Films for Gas Separations

MARK R. ANDERSON, BENJAMIN R. MATTES, HOWARD REISS,* RICHARD B. KANER*

Permeabilities for a series of gases through free-standing films of the conjugated polymer polyaniline are reported. A remarkable selectivity has been achieved for important gas pairs including hydrogen-nitrogen, oxygen-nitrogen, and carbon dioxide–methane. The selectivity values of 3590 for H_2/N_2, 30 for O_2/N_2, and 336 for CO_2/CH_4 surpass the highest previously reported values of 313, 16, and 60 for the nonconjugated polymers poly(trifluorochloroethylene), cellulose nitrate, and a fluorinated polyimide, respectively. The process for tailoring gas selectivity of a polyaniline membrane involves first enhancing the permeabilities of gases with small diameters [<3.5 angstroms (Å)] by doping and undoping the polymer film with counterions of an appropriate size. High selectivities are then achieved by decreasing the permeabilities of larger gases (>3.5 Å diameter) through controlled redoping of the polymer. The permanent morphological changes induced in this conjugated polymer system and others indicate the potential for development of universal membranes for gas separations.

THE ABILITY TO SEPARATE MIXTURES of gases is essential for a wide variety of industrial applications (*1*). In the manufacturing of chemicals, unreacted hydrogen can be recovered from waste gas streams and recycled. Low-grade natural gas can be purified by the removal of carbon dioxide and hydrogen sulfide to reduce pollution. Carbon dioxide can then be reused in tertiary oil recovery. Air can be separated into oxygen and nitrogen. Valuable nonrenewable resources such as helium can be recovered and recycled.

Membrane-based gas separations have tremendous potential as energy-efficient alternatives to cryogenic separations. Within the last decade a number of membrane systems have been introduced commercially (*2, 3*). The synthesis of new polymeric materials (*4, 5*) and the development of asymmetric membranes, in which a thin skin of polymer with high gas selectivity is grown on a porous structural support (*1, 6–8*), have made this possible. The thin polymer skin, which ranges in thickness from a few hundred to a few thousand angstroms, is crucial to any membrane separation process. Current membrane systems have limited applications because the morphology of a polymer film is difficult to predict prior to the manufacturing process and cannot be adjusted consistently once the film is formed. We report a new approach to gas membrane separators in which we use a class of polymers whose morphologies can be precisely controlled after synthesis to optimize a particular separation.

Dopable conjugated polymers, of which conducting polymers constitute a subgroup, form a relatively new class of organic materials that have been studied extensively for their electrical properties since the first doping experiments were reported on polyacetylene in 1977 (*9*). Conducting polymers (including polypyrrole, polythiophene, polyparaphenylene, polyaniline, and their derivatives) have potential for use in a wide variety of electronic devices (*10–13*). Gas separation represents a new area of application for these materials. Although the features that predispose these polymers to being conductive may still be important, their electrical conductivity plays only an indirect role. The doping process that makes these materials conductive allows precise changes to be made in their morphology.

Polyaniline, $(C_6H_4NH)_x$, is a desirable membrane material because of its air stability in both neutral and doped forms, its excellent processibility and rheological properties, and its simple acid-base doping chemistry in aqueous solution. The polymer powder is made directly from a relatively inexpensive monomer. Furthermore, conventional polymer processing techniques yield high-quality, mechanically robust films.

Polyaniline, in the emeraldine oxidation state,

$$[(-C_6H_4-NH-C_6H_4-NH-)_{0.5}$$
$$(-C_6H_4-N=C_6H_4=N-)_{0.5}]_x$$

is synthesized by chemical oxidation of aniline (*14*). The polymer powder was purified by successive wash cycles with aqueous acid (1.0 M HCl) and base (0.1 M NH_4OH), each cycle followed by filtration and vacuum drying. The emeraldine base was ground to a fine powder, swelled with tetrahydrofuran, and dissolved in *N*-methyl pyrrolidinone (NMP) (5.0% w/v). The films were formed by spreading the viscous, homogeneous solution onto glass plates with a casting bar. The polymer-coated plates were cured at 135°C for 1 to 3 hours in a drying oven. The resulting ~0.1-mm-thick films were separated from the glass plates by immersion in

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Department of Chemistry and Biochemistry and the Solid State Science Center, University of California, Los Angeles, Los Angeles, CA 90024–1569.

*To whom correspondence should be addressed.