Reports

Plate Tectonics 2.5 Billion Years Ago: Evidence at Kolar, South India

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The Archean Kolar Schist Belt, south India, is a suture zone where two gneiss terranes and at least two amphibolite terranes with distinct histories were accreted. Amphibolites from the eastern and western sides of the schist belt have distinct incompatible element and isotopic characteristics suggesting that their volcanic protoliths were derived from different mantle sources. The amphibolite and gneiss terranes were juxtaposed by horizontal compression and shearing between 2530 and 2420 million years ago (Ma) along a zone marked by the Kolar Schist Belt. This history of accretion of discrete crustal terranes resembles those of Phanerozoic convergent margins and thus suggests that plate tectonics operated on Earth by 2500 Ma.

HETHER PLATE TECTONICS OPerated in the first 2000 million years of Earth history remains controversial and has broad implications. For example, interpretations of the mechanisms by which Earth's continental crust evolved provide a basis for understanding the early histories of other planets and why continents either never formed or were arrested in a primitive state on the moon and Mars and possibly on Venus. In this report we describe isotopic and geologic evidence for the growth of the early continental crust in south India. We propose that by at least 2500 Ma the continental crust in this area had begun to grow by mechanisms indicative of plate tectonic activity.

The Dharwar Craton of southern India (1, 2) is dominantly composed of gneiss and supracrustal belts, referred to as schist belts, that have undergone greenschist- to granulite-grade metamorphism. Metamorphic grade increases to the south. All of the felsic gneissic rocks in the Dharwar Craton, independent of age or origin, are known collectively as the Peninsular Gneiss.

The Dharwar Craton is thought to have formed as a terrane of 3400 to 3000 millionyear-old granitic gneiss (3) that was rifted between 3000 and 2600 Ma and overlain by correlatable successions of supracrustal rocks (now the schist belts). Intracrustal compression and crustal melting at 2600 to 2500 Ma produced zones of high strain, deformed the

duced a suite of crustally derived, highpotassium granites (1-8). These models for the evolution of the Dharwar Craton have been based mainly on

data from the western part of the craton. The eastern part is made up largely of granodioritic to granitic gneiss. The few schist belts are smaller and more narrow than those in the west. The eastern schists are mostly mafic metavolcanic rocks, whereas the western schists are mostly metamorphosed sedimentary rocks.

schist belts, caused regional, transgressive,

granulite-grade metamorphism, and pro-

The north-south trending Kolar Schist Belt is one of the easternmost schist belts of the Dharwar Craton (Fig. 1). This belt is 3

Fig. 1. Geologic map of the eastern part of the Dharwar Craton modified from Raith et al. (2). The approximate location of the transition between the amphibolite- and granulite-grade terranes in the craton is marked by the dashed line labeled A-G. The Kolar Schist Belt (KSB in the inset map of India) and the proposed Kolar suture trend northsouth; proposed northern and southern extensions of the suture are marked by the dotted line. These are the approximate locations of the zones of Archean high strain (26); N is the

to 4 km wide by 80 km long and consⁱ of tholeiitic and komatiitic rocks wi inor metamorphosed iron formation and graphitic slate. These rocks have been metamorphosed to middle amphibolite grade (9). The contact zones with the surrounding gneisses are highly sheared, locally mylonitized, and characterized by the development of quartz-muscovite schists in the gneisses (10).

The rocks in the Kolar Schist Belt have been subjected to four phases of folding (F_1 to F_4) and to a late F_2 -stage ductile shearing event (11, 12). The first two generations of tight to isoclinal folds and late-stage ductile shearing are related to an east-west subhorizontal compression event (11). The F_3 and F_4 folds are unimportant on a regional scale.

Foliations in the gneisses on both sides of the Kolar Schist Belt are parallel to the steeply dipping north-south foliation in the schist belt. The orientation and sense of shear of conjugate shear zones in the gneisses also suggest that maximum compression was nearly east-west and subhorizontal (11).

Rajamani *et al.* (13) suggested that the komatiites in the schist belt were derived from depths of greater than 100 km, but that those on the east side were derived from a light rare earth element (LREE)–enriched source and those on the west side from a LREE-depleted source. The tholeiitic amphibolites of the Kolar Schist Belt are not related to the komatiitic amphibolites, either by derivation from a common source or by fractional crystallization (13).

The komatilitic amphibolites in the western part of the Kolar Schist Belt all may be related to a common mantle source by vary-



location of the Nilgiri Hills; KR is the location of Krishnagiri; and B is the location of the Biligirirangan Hills, the study areas of other workers (25) discussed in the text. The gneisses near Krishnagiri are isotopically similar to those on the east side of the Kolar Schist Belt; those in the Nilgiri Hills are isotopically similar to those on the west side of the Kolar Schist Belt. The crust as far as 200 km to the east of the Kolar Schist Belt may be juvenile crust that formed at about 2500 Ma (27); in contrast, the crust to the west of the schist belt, although having some rocks derived from the mantle \sim 2600 Ma, includes some much older (3400 to 3000 Ma) continental rocks.

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Table 1. Characteristics of terranes adjacent to the Kolar Schist Belt; *t* indicates reference age at which initial isotopic ratios are calculated; this age is based on U-Pb zircon age determinations.

Age or isotopic ratio	Western gneiss terrane	Eastern gneiss terrane
Zircon ages	2630 to 2550 Ma	2530 Ma
Sphene ages	2553 to 2550 Ma	2521 to 2500 Ma
$\epsilon_{Nd}(t)$	+2 to -7.5	+4.5 to 0.0
⁸⁷ Sr/ ⁸⁶ Sr _i *	0.7025 to 0.7230	0.7013 to 0.7014
Model µ ₁	8.5 to 11	8.0 to 8.2
Potassium-feldspar-whole rock Pb-Pb ages	~2420 Ma	~2420 Ma

*Initial ratio.

Fig. 2. ²⁰⁷Pb/²⁰⁴Pb versus ²⁰⁶Pb/²⁰⁴Pb data for amphibolites (whole rocks) and galena (16) from the schist belt, and eastern (E) and western (W) gneisses (leached potassium-feldspars) of the Kolar Schist Belt area. Six of the western tholeiitic amphibolites from one outcrop (filled triangles) define an isochron age of 2730 ± 160 Ma. The various amphibolite units lie in discrete (nonoverlapping) fields, thus their differences are not simply the result of variable contamination by galena Pb. The high 207Pb/



²⁰⁴Pb values of feldspars from the western gneisses indicate that there was a long-term history of high U/Pb ratio before 2500 Ma; the feldspars from the eastern gneisses lack this signature.

ing, but small, extents of partial melting (13); Sm-Nd data for various samples plot close to an isochron with an age of 2690 ± 140 Ma (14). This age is similar to a Pb-Pb age of 2730 ± 160 Ma [single stage $\mu = 7.5 (15, 16)$ for six samples from one outcrop of the western tholeiitic amphibolite (16) (Fig. 2). High, but heterogeneous, initial ¹⁴³Nd/¹⁴⁴Nd ratios [ϵ_{Nd} from +2 to +8 at 2700 Ma (14, 17)] for the western komatiites indicate that the source origin of these rocks had a long-term history of LREE depletion. The lack of covariation between ε_{Nd} and Sm/Nd ratios for these samples allows significant crustal contamination of the komatiite magmas to be ruled out. If the 2700 Ma age represents the time of magmatism, which we propose, then the mantle source had considerable Nd isotopic heterogeneity by that time (14). The Nd data from other amphibolite units of the Kolar Schist Belt are similarly internally heterogeneous.

The Pb isotope data for the four amphibolite units in the Kolar Schist Belt (western komatilites, western tholeiites, eastern komatilites, eastern tholeiites; Fig. 2) support the suggestion that the sources of these different units had separate histories (Fig. 2). This interpretation is also indicated by major and trace element (13) and Nd isotope (14) data. The Pb isotope compositions of galena in the schist belt (18) are similar in composi-

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tion to those of the least radiogenic potassium-feldspars from the western gneisses (19) (Fig. 2). These data suggest that Pb of this composition was introduced into the belt, probably during shearing or Au mineralization. Although some of the scatter in the Pb isotope ratios for the amphibolites may be explained by contamination by extraneous Pb, such contamination probably could not have produced the different groupings of the Pb compositions of the tholeiites and komatiites (Fig. 2). Such a separation supports the interpretation that the western komatiitic and tholeiitic amphibolites were derived from different sources. The LREEdepleted, western komatiitic amphibolites may represent Archean equivalents of ocean ridge basalts derived from Archean asthenosphere, and the interlayered tholeiitic amphibolites were derived from Archean lithosphere that in terms of U and Pb, evolved separately from the komatiite source. The LREE-enriched eastern komatiitic amphibolites have high positive ϵ_{Nd} values (14), which indicate that their source region had a long-term depletion in LREE and must have been enriched just before formation of the komatiites. These eastern komatiites also have Pb isotope characteristics significantly different from those of the western komatiitic and tholeiitic amphibolites (Fig. 2) and may have been the Archean equivalent of ocean island or island arc basalts.

In summary, the amphibolites of the Kolar Schist Belt were formed from melts derived from diverse mantle sources with varied, but pronounced, records of depletion in the LREE. The U-Pb histories of these mantle sources were also variable and distinct. Whereas some of the Pb isotopic variation may be due to contamination by older crustal Pb, the distinct grouping of the amphibolite Pb data suggests that the differences among the groups are not a result of melts having appreciably interacted with older continental crust. The lack of correlation between ϵ_{Nd} and Sm/Nd ratios of these amphibolites also indicates that there was little, if any, assimilation of older continental crust Nd. These data suggest that the melts were emplaced in an oceanic setting. The various units of amphibolites are now juxtaposed, but their contacts are apparently tectonic. The various amphibolites may therefore be metamorphosed fragments of a closed Archean ocean or back-arc basin that were brought together between the two gneiss terranes.

Gneisses of monzodioritic to granitic composition on the western side of the Kolar Schist Belt have U-Pb zircon ages of 2632 ± 7 , 2610 ± 10 , and 2553 ± 2 Ma (20). The major and trace element characteristics of these gneisses suggest that the parental melts were mostly mantle-derived, high-magnesium andesite magmas (21) that represent primary additions to the crust. As shown by the evolved initial ratios of Sr, Nd, and Pb (Table 1) these magmas were, however, contaminated by much older, LREE-enriched, granitic crust (19). This crust may be represented by a felsic banded gneiss, which occurs sporadically as enclaves in the western gneisses and is the least abundant type among the four major gneiss units studied to the west of the schist belt. This gneiss appears to be a partial melt of a crustal parent (21) that formed by at least 3200 Ma, as indicated by U-Pb data on zircon, whole-rock Pb, Nd, and Sr isotopic ratios (Table 1), and potassium-feldspar isotopic Pb data (20).

In contrast, east of the schist belt the gneisses show no Pb, Sr, or Nd isotopic evidence for a much older basement (19) (Table 1 and Fig. 2). Although these gneisses are relatively evolved granodiorites with Mg/(Mg + Fe) of less than 0.50, and probably were not derived directly from mantle sources (20, 21), the isotope data indicate that the U/Pb or Sm/Nd ratios of their sources evolved similarly to those of mantle until no more than 100 million to 200 million years before their emplacement at 2532 ± 3 Ma (20). Balakrishnan and Rajamani (19) suggested that the magmas parental to the eastern gneisses may have

formed by fractionation of mantle-derived, high-Mg andesitic magmas or melting of such rock types.

The eastern gneiss terrane was most likely separated from the western terrane until \sim 10 to 150 million years after the formation of the gneisses east of the Schist belt. Sphene U-Pb ages from gneisses on the east side of the Kolar Schist Belt, possibly recording cooling from magmatic or high-grade metamorphic temperatures, range from 2521 ± 1 to 2501 ± 4 Ma (20). The oldest of these is 32 million years younger than U-Pb sphene ages from western gneisses (2553 \pm 2 Ma) only 7 km away across the schist belt. An ⁴⁰Ar-³⁹Ar muscovite plateau age of 2420 ± 12 Ma from sheared gneisses on the western margin of the schist belt, and potassium-feldspar-whole rock Pb-Pb ages of 2350 to 2490 Ma from gneisses on both sides of the schist belt probably record cooling after metamorphism and deformation associated with the collision of the two gneiss terranes sometime between 2530 and 2420 Ma (20).

This interpretation contradicts earlier models suggesting that the gneisses of the Dharwar Craton were predominantly formed between 3400 and 3000 Ma (1, 8). Rather, our isotopic data indicate that a



Fig. 3. Block diagram schematically showing the evolution of the Kolar Schist Belt and surrounding gneisses. The age of older continental basement on the west is based on inherited zircons, isotopic signatures, and sporadic fragments of older crust occurring as xenoliths and tectonic inclusions in the western gneisses. The age of the schist belt is based on Sm-Nd, Pb-Pb, and Rb-Sr isochrons. The ages of gneisses are U-Pb zircon ages. The minimum age of the inferred suture (2420 Ma) is based on ⁴⁰Ar-³⁹Ar mineral and Pb-Pb mineral-whole rock ages.

significant portion of the late Archean gneisses west and east of the Kolar Schist Belt were new additions to the continental crust and not products of remelting of the 3400 to 3000 million-year-old gneiss terrane

We propose that the Kolar Schist Belt is a suture zone (boundary between two or more terranes) marking the site of accretion of juvenile continental crust and intervening oceanic fragments along a dominantly north-south trending belt (Fig. 3). At about 2700 Ma, the volcanic rocks of the eastern and western parts of the Kolar Schist Belt were extruded at two different oceanic sites. At that time only the old basement to the western gneisses had formed, but it was not necessarily in its present location with respect to the schist belt. The eastern gneiss terrane had not yet formed. Between 2630 and 2530 Ma the intrusive granitic rocks now exposed at the surface on the western and eastern sides of the belt were formed at separate sites. Between 2530 and 2420 Ma the two amphibolite and two gneiss terranes came together, causing compression and eventual shearing of the rocks in the belt and the surrounding gneisses. This deformation may have resulted from oblique convergence or from separate convergence and strike-slip motion. A model similar in style to the one presented here has recently been proposed for the Archean terranes in the Tre Brødre-Buksefjord area of southwest Greenland (22).

A possible Phanerozoic analogue to the tectonic setting of the Dharwar Craton is the Mesozoic-Cenozoic margin of the North American Cordillera, where fault-bounded, allochthonous terranes apparently were accreted by plate convergence (23). Terrane boundaries are commonly marked by belts of disrupted ophiolite suites, consisting of ocean floor sedimentary rocks, pillow basalts, sheeted dike complexes, gabbros, and peridotites. In older accretionary settings these boundaries may be represented by belts of mafic metavolcanic rocks, like the Kolar Schist Belt, rather than by entire ocean crust sections (24).

Because of the large differences between the sources for the gneiss terranes east and west of the Kolar Schist Belt, larger terranes (greater than hundreds of square kilometers) could have been accreted. Similar gneisses are located about 100 km to the south, approximately along the zone of Archean high finite strain (26) that extends in a north-south direction along the Kolar Schist Belt (Fig. 1) and near the transition to granulite-grade rocks (4, 5). The Rb-Sr and Sm-Nd ages (25) and initial ratios of Sr, Nd, and Pb from these gneisses suggest that they were derived from the mantle at about 2500

Ma. Additionally, granulite-grade gneisses ~200 km east of the Kolar Schist Belt near Madras have Nd isotopic ratios at 2500 Ma similar to those of the gneisses east of the Schist Belt (27), and thus may also represent juvenile latest Archean crust.

Gneisses from near the high-low grade transition zone in the western Karnataka Craton (Biligirirangan and Nilgiri hills, Fig. 1) have Pb, Sr, and Nd isotopic signatures (25) similar to those of the gneisses west of the Kolar Schist Belt, indicative of significant contribution from older (greater than 3000 Ma) crust. The suture may, therefore, extend from the Kolar Schist Belt southsouthwest to the southern part of the craton. This suture, and the granulite-grade metamorphism in the southern part of the craton, which also formed at about 2500 Ma (1), may have been associated with the collision of Archean continental plates. More studies will be required to determine if this part of the Dharwar Craton is representative of the style of growth of continental crust in the Late Archean.

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The Axial Oxygen Atom and Superconductivity in YBa₂Cu₃O₇

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Changes in the copper K-edge x-ray absorption spectrum of $YBa_2Cu_3O_7$ across the critical temperature indicate that, accompanying the superconducting transition, the mean square relative displacement of some fraction of the Cu2–O4 bonds becomes smaller or more harmonic (or both), that there may be a slight increase in the associated Cu1–O4 distance, and that electronic states involving these atom pairs become more atomic-like. If there is an association between the superconductivity and this lattice instability, then the bridging axial oxygen is of central importance in determining the high transition temperature of $YBa_2Cu_3O_7$. Because this structural perturbation will affect the dynamic polarizability of the copper oxygen sublattice, it is consistent with an excitonic pairing mechanism in these materials.

ESPITE THE INTENSITY WITH which the superconducting cuprates have been studied since their discovery (1), direct information about changes in their atomic and electronic structures in the vicinity of the transition temperature is largely lacking, and the mechanism of superconductivity in these materials is still uncertain (2). Copper K-edge x-ray absorption spectroscopy (XAS) measurements have shown that chemical modification of YBa2Cu3O7 (for example, by doping) results in small differences in the x-ray absorption near-edge structure (XANES) indicative of corresponding changes in structural properties (3). Although these differences are quite subtle, we have recently found that they can be amplified by subtracting the XANES of the modified compounds from that of a high-quality, undoped sample (4). Features in these difference spectra are easily identified with respect to the assigned transitions in the spectrum of YBa₂Cu₃O₇ (5, 6) and their magnitudes show a consistent trend with the dopant concentrations. The sensitivity and utility of this difference spectrum approach suggested its application to the examination of the temperature dependence of YBa₂Cu₃O₇, as reflected in the XANES. In this paper, we report direct evidence for specific changes in

the atomic structure and electronic configuration accompanying the transition to the superconducting state.

We have examined two samples of YBa2-Cu₃O₇, prepared from Y₂O₃, BaCO₃, and CuO by conventional ceramic procedures. Samples 1 and 2 were both single phase (as determined by x-ray and electron diffraction), both showed superconducting transition temperatures (onset) of 92 K, and they had oxygen stoichiometries of, respectively, 6.97 and 6.98 (thermogravimetric analysis). The superconducting volume fraction (after a demagnetization correction) of sample 1 was 0.97 at 7 K, whereas that of sample 2 was only 0.35. Certain aspects of the diffraction patterns of sample 2 suggested less than perfect order in the c direction. The differences in the preparations of these two samples were that sample 1 was fired at 950°C, slowly cooled, and given a long anneal in O₂ at 450°C, whereas sample 2 was fired at 900°C and then furnace-cooled in O₂ to room temperature directly. Amounts of these samples calculated to produce an absorbance of unity over the copper K edge were used for these measurements. All XAS data were recorded at the Stanford Synchrotron Radiation Laboratory on beam line I-5 under dedicated operating conditions (3-GeV electron energy, 50-mA beam current, no positrons). The inflection point of the first feature in the copper metal spectra used for calibration was defined as 8980.3 eV. The effects of background variations on the normalized difference spectra were compensated for by performing small (0 to 0.7%) adjustments to maximize the overlap of the two spectra from 8980 to 8982 and 9023 to 9030 eV.

The XANES spectrum of sample 1 is shown in Fig. 1. Below the ionization threshold at around 9000 eV, features in the XANES labeled A to E (5, 6) correspond to transitions from the core level of the absorbing atom to the bound, localized electronic states of the system (5-11). Above the ionization threshold, the XANES contains discrete transitions to more delocalized and multiple-scattering types of final states in addition to the low k region of the extended x-ray absorption fine structure (EXAFS). The energies and intensities of these types of resonances, originating in the interaction of the low kinetic energy photoelectron with the potential of the neighboring atoms, are very sensitive to the exact structure of the local cluster around the absorbing atom (7, 9). This XANES spectrum, extending about 50 eV above the onset of absorption, therefore simultaneously probes both the electronic states of the copper atoms and the atomic structure around them.

Difference spectra have been computed for sample 1 for five pairs of temperatures up to 150 K (Fig. 2). In addition to changes in the intensities of the localized transitions A, B, C, and D, a pattern of oscillations with extrema at 9000, 9003, 9006, 9010, 9014, and 9020 eV is evident in the structuresensitive region. The iteration of this pattern and the virtually identical shapes of the spectra obtained for samples 1 and 2 across the transition temperature T_c indicate that these spectra reflect the same distinct lattice instability. This spectral pattern was not



Fig. 1. The Cu K XANES of YBa₂Cu₃O₇ at 11 K. Transitions to discrete, localized final states are indicated by arrows and assigned based on (5), MS = multiple scattering-type transition. Alternative assignments are discussed in (16). Features corresponding to some of these transitions are more difficult to see in this powder spectrum than in those from oriented samples or in the difference spectra.

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