

Archean biogeochemical cognizance from Dharwar Craton, India-A review

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Abstract

The Banded iron formations (BIFs) and Manganese formations of Chitradurga, Shimoga and Sandur greenstone belts of Dharwar Craton, associated with the stromatolitic carbonates, carbonaceous phyllites and shales along with gold mineralization, are best geological entities to evaluate the Archean biogeochemical processes and transformation of a habitable Earth. The geochemical anomalies along with C, O and S isotopic signatures of stromatolitic carbonates, carbonaceous phyllites and sulphidic BIFs reflect on biogenic signatures, fluctuating Archean Ocean temperatures from 25-75°C and anoxic to euxinic redox conditions. The U-Pb detrital zircon ages of these stromatolitic carbonates indicate 3.5 to 2.6 Ga whereas the carbonaceous shales indicate 3.2 – 2.2 Ga source reflecting the transportation of organic matter to the ocean basin during the growth of stromatolitic carbonates. The gold content of carbonaceous phyllites and sulphidic BIFs indicates hydrothermal source. The O₂ produced due to stromatolitic activity has deposited Mn and Fe of the Archean oceans as BIFs and Mn formations. The biogenic matter of the stromatolites along with other siliciclastic material, gold and sulphides derived from the volcanic activity, formed as carbonaceous shales in the ocean basin along with sulphidic BIFs in deep water euxinic conditions. The comprehensive geological, geochemical including isotopic studies on these rock types collectively indicate the interaction of lithosphere-hydrosphere-atmosphere-biosphere in the Archean oceans which paved the way for the advanced forms of life.

Keywords: Archean, Dharwar Craton, Biogeochemical, stromatolites, Carbonaceous Phyllites

Introduction

The evolution of life on planet Earth is interlinked to the secular changes in the environment which were predominantly contributed by a combination of biological and geodynamic processes (Lepot, 2020). The initiation of biogeochemical processes on the planet Earth is one of the most significant aspect which paved the way to the evolution of lithosphere, atmosphere, biosphere and hydrosphere thereby played a vital role in the deposition of various mineral deposits that is responsible for a sustainable Earth. Among these mineral deposits, the iron, manganese and gold deposition have a link with the biogenic activity during the Precambrian time. Recent studies imply that the surface oxygen levels during the Archean were extremely low (10^{-6} times), N_2 levels were similar, CO_2 and CH_4 levels were ~10 to 2500 and hundreds to thousands of times higher compared to present atmosphere (Catling and Zahane, 2020). Minor changes in atmosphere began with anoxygenic metabolic pathways but the exact time of beginning of oxygenic photosynthesis and its domination over anoxygenic photosynthesis is still debated (Homann, 2019). Oxygenic photosynthesis was more prevalent during 2.4 and 2.3 Ga and the atmosphere was flooded with oxygen produced by the cyanobacteria (Knoll et al., 2016). This major transition in atmosphere was coupled with sudden disappearance of mass-independent fractionation (MIF) of sulfur isotopes. Therefore, the Precambrian atmosphere, covering one-third of the Earth's geological history, marks many important climatic and atmospheric events and diversification of primitive life forms which can be studied in the sedimentary successions.

The Precambrian banded iron formations (BIFs) are very significant and world's largest iron producers and associated with manganese formations, stromatolitic carbonates and carbonaceous phyllites. The sulphide facies iron formations and the carbonaceous phyllites have gold mineralization which has been mined from few areas (Sindhuja, 2021). In this communication, the authors evaluate the influence of biogenicity in the deposition of iron-Mn and Au mineralization from selected greenstone belts of Dharwar Craton which are the result of interaction between lithosphere-atmosphere-hydrosphere and biosphere.

Geological Background

The Archean Dharwar Craton has well developed granite-greenstone successions in which some of the sedimentary rocks have traces of biogeochemical processes. One of the most important aspect of Dharwar geology lies with the lithological association of few greenstone belts which have abundant iron and manganese deposits along with biogenic structures such as stromatolitic

carbonates carbonaceous phyllites and cherts (Manikyamba et al., 2017; Khelen, 2018; Sindhuja, 2021). Among them, the Chitradurga, Shimoga and Sandur greenstone belts are noteworthy due to the presence of various types of volcanic and sedimentary rocks with iron, manganese and gold mineralization. Irrespective of their presence in the western or eastern sectors of Dharwar Craton, these greenstone belts contain important information to understand the biogenic activity and its influence on the mineralization. The Vanivilas Formation of Chitradurga greenstone belt consists of chemical sediments such as limestones, banded manganiferous chert and phyllites and banded iron formation (BIFs). The stromatolitic carbonates are exposed at Bhimasamudra, Marikanve, Dodguni areas of this belt (Khelen et al., 2019 a, b). The carbonaceous phyllites are present at G.R. Halli, Tekkalavatti and also in Gadag which is the northern continuation of the Chitradurga belt. Sulphide facies BIFs are exposed at Chikkasiddavanahalli and Ajjanahalli areas which were mined for gold earlier (Raju, 2009; Khelen, 2018; Sindhuja, 2021). The Sandur greenstone belt has vast iron and manganese deposits in which the Yeswanthapur Formation consists of stromatolitic carbonates (Khelen, 2018). Carbonaceous phyllites and sulphidic BIFs are closely associated in the Donimali Formation (Sindhuja, 2021). The Joldhal Formation of Shimoga greenstone belt has stromatolitic carbonates, ferruginous cherts, carbonaceous phyllites and cherts which are associated with volcanic rocks. The sulphide facies BIFs of Ganajur, Karajgi and Palvanahalli consists of gold mineralization (Ganguly et al., 2016). The association of BIFs, Mn-formations, stromatolitic carbonates, sulphide facies iron formations and the carbonaceous phyllites is very significant in these greenstone belts which provide evidence on Precambrian biogenic activity and its influence on atmosphere, hydrosphere and thereby the lithospheric processes collectively.

Hydrothermal influx into the Archean oceans

The iron and manganese formations are one of the most important rock types which unravel many significant events that have not been repeated in the geological time scale and provide an understanding about the composition of the Archean oceans. In the modern oceans, the oceanic ridge hydrothermal and fumarolic activity is the main source for the metalliferous deposits. The REE and Nd isotopic data of the Archean and Proterozoic BIFs demonstrated that hydrothermal solutions derived from the deep and depleted mantle is the main source for iron (Derry and Jacobson, 1990). Campbell et al. (1988) identified Mn anomalies in the ocean water and high Mn content in the metalliferous sediments of East Pacific Rise and identified the dispersion of hydrothermal solutions in the ocean currents above the ridge axis upto an extent of 100-200 m. It has been quantified that ~1.5-90% of total Mn of ocean has been supplied from hydrothermal solution. The REE patterns especially the La enrichment, positive Eu anomalies

which is also observed in the Mesozoic cherts supports that silica has also been supplied through the hydrothermal activity at MOR which is evidenced by Si anomaly at Gulf of California (Campbell et al., 1988) and anomalously high dissolved Si in the Red Sea, Afar rift and Guaymas basin (~175 Mmol/kg). Influence of hydrothermal vents in the deposition of cherts interlayered with the BIFs of Archean Abitibi greenstone belt, Canada display Eu/Eu*

~70 similar with the high T hydrothermal fluids (Thurston et al., 2012). All these evidences collectively indicate that the Fe, Mn and Si along with metal sulphides including gold of the BIFs and Mn were supplied through the Archean mid oceanic ridge (AMOR) hydrothermal solutions. The depleted REE patterns along with La enrichment and positive Eu anomalies reflect the hydrothermal signature in the BIFs of Sandur and Chitradurga belts which is also evidenced from other cratons (Manikyamba et al., 2017; Mukhopadhyay, 2020). The sulfides in these BIFs have a direct connection with the Archean volcano-exhalative process. As stromatolitic carbonates and carbonaceous shales were also deposited in the same ocean water, their trace element ratios also indicated the traces hydrothermal signatures (Khelen, 2019 a; Sindhuja, 2021).

Archean atmosphere and ocean composition

Due to sporadic evidences present in the rock record, evaluating the composition of hydrosphere, atmosphere and lithosphere before the initiation of biosphere is one of the most significant and challenging aspect (Schoonen and Smirnov, 2016). The hot primitive Earth soon after its formation (~ 4.5 Ga), settled within a period of 20-100 Ma with a liquid water and CO₂ dominated atmosphere which was initially 100 atm and gradually decreased to 1 atm

. The high CO₂ contributed to high ocean temperatures (>100 °C) with > 1 atm. atmospheric pressure appears to have produced significant amount of organic compounds. The high dissolved CO₂ in oceans have generated the organic compounds which initiated the biosphere. Clays formed as weathering products have adsorbed, concentrated and protected the biomolecules due to their layered structures. The Archean ocean composition is poorly constrained which is mainly dominated by volcano-exhalative activity and rock-water interactions (Raudsepp, 2012). Atmospheric CO₂ was very high, pH was >6.5 and the temperatures were >57 °C and the salinity was comparable with the modern seawater (Holland and Kasting 1992; Grotzinger and Kasting, 1993). Metal redox states were prevalent in the Archean oceans due to anoxic ocean water and atmospheric conditions.

The black smoker hydrothermal vents present in the ocean floor emit high temperature fluids of 250-400 °C along with reduced transitional metals, high CO₂, H₂S which result into an

acidic pH (~2-3). These vent solutions when they come in contact with cool and alkaline ocean water result into thermal gradient and redox conditions which are suitable for the metabolic reactions. Iron sulphide minerals, CH₄, H₂ formed in these areas create suitable conditions for the metabolic enzymes. The white smoker hosted by ultramafics at the ocean floor will have milder temperatures of 60-90 °C, alkaline pH (~9-11) and precipitate Ca and Mg carbonates. These vents play a vital role in creating the thermal and chemical gradients that are necessary for the growth of microbiota (Holland, 2002).

Evolution of biosphere during Archean-Influence of stromatolites

After diminishing the extreme conditions of Hadean Earth, the 'Habitable trinity' existed and initiated the biological processes during the Archean era (Maruyama and Santosh, 2017). 3.5 Ga life processes is evidence from the Pilbara Craton, Australia and Barberton greenstone belt, South Africa (Nesbitt and Fowler, 1999). The Global Oxygenation Event (GOE) proposed at ~2.4 Ga is 300 Ma later than the Neoproterozoic oxygenation peak recorded through the predominant BIF deposition associated with the occurrence of stromatolitic carbonates and Mn formations which is evidenced from the Dharwar Craton (Fig. 1C). The increase in atmospheric O₂ was dependent on the balance between its production and consumption and the sources include the burial of organic carbon and occurrence of pyrite. All these evidences are preserved in the Dharwar Craton with the production of O₂ through the stromatolitic activity, its sink as Fe, Mn deposits, the burial of organic carbon through carbonaceous shales/phyllites which are closely associated with the sulphidic cherts/BIFs (Manikyamba et al., 2017). The Chitradurga, Shimoga and Sandur greenstone belts meet all these parameters reflecting the interplay of atmosphere, hydrosphere and lithosphere for the evolution of biosphere in the Dharwar Craton.

The abiotic oxidation of Fe by UV light during the Archean time cannot be considered, as the experimental results suggest the formation of greenalite or siderite (Konhauser et al., 2007). Cloud (1973) proposed the oxidation of ferrous iron of anoxic ocean through the O₂ produced by cyanobacteria. According to Allen and Martin, (2007) manganese and calcium acted as catalysts in the production of oxygen through photosynthesis. Initially four electrons of manganese and one calcium cluster as Mn₄Ca and attack on two H₂O molecules by utilizing the sun light from nature and release O₂ in which Mn played a vital role in the absorption of light. Therefore, the emergence of Archean biogenic processes on the planet Earth has brought many significant changes in the atmosphere, hydrosphere, O₂, C, S, N, Fe and Mn cycles associated with various geological processes.

Microfossils are rare in the Precambrian stromatolites due to alkalinity gradient between the bulk ocean water and cyanobacterial mats (Arp et al., 2001) which are common in Paleozoic and Mesozoic rocks. Due to high atmospheric CO₂ and dissolved inorganic carbon concentration during the Precambrian time, carbonate concentration is throughout the mat which are preserved as stromatolites without individual cells (Raudsepp, 2012). Stable isotopes and trace element compositions of sedimentary rocks provide evidence of early life on Earth that are consistent with a biological influence on their geochemistry. Predominantly negative $\delta^{13}\text{C}$ of Sandur (-1.61 to 0.01‰), negative to positive $\delta^{13}\text{C}$ of Chitradurga (Bhimasamudra= -0.11 to 1.35‰; Dodguni= -1.30 to 0.31‰); Marikanve = -2.53 to 1.06‰) and predominantly positive $\delta^{13}\text{C}$ of Shimoga (-0.30 to 1.29‰) stromatolites endorse a steady growth of bioproductivity in these greenstone belts thus constrain gradual increase in ocean anoxia, increased organic carbon burial and nutrient supply in the Archean oceans (Khelen, 2019). Consistent depletion in $\delta^{18}\text{O}$ values of Sandur (-20.95‰ to -12.24‰), Bhimasamudra (-14.54‰ to -11.87‰), Dodguni (-14.90‰ to -9.96‰), Marikanve (-18.70‰ to -15.19‰) of Chitradurga and Shimoga (-9.85‰ to -7.72‰) stromatolites collectively indicate increased sea water temperatures from 25-75°C and the influence of hydrothermal solutions (Khelen, 2019) which is supported by earlier studies on cherts and dolomites of Shimoga belt (Sharma et al., 1994).

The U-Pb detrital zircons of Dharwar stromatolitic carbonates yield an age of 2650 ± 38 Ma to 3508 ± 29 Ma suggesting the Paleo to Neoproterozoic provenance reflecting the proximal continental crust of the Sargur and Dharwar Groups (Khelen et al., 2019 b). These studies indicate that the stromatolitic growth took place from 3.5 Ga onwards and continued upto 2.6 Ga wherein sufficient O₂ levels reached by Neoproterozoic time resulted in the deposition of Mn and Fe in the Dharwar Craton that are preserved in various greenstone belts.

Carbonaceous shales and anoxic environment

According to Holland (2003), presence of paleosols, lack of red beds, occurrence of detrital uraninite and pyrite in the sedimentary rocks indicate low O₂ content during the Archean. Besides, the mass independent fractionation of sulphur isotope (MIF-S) record indicates that O₂ content in the Archean was $< 10^{-5}$ PAL (present atmospheric level; Pavlov and Kasting, 2002) and the rise of O₂ was above 10^{-5} between 2.45 – 2.32 Ga which is considered as GOE (Bekker et al., 2004).

Carbonaceous shales are enriched in organic carbon contents, serve as natural archives of primeval life and provide key information on the metabolic pathways that led to the origin of earliest life forms (Schidlowski, 1987). They also have profound implications on the global

biogeochemical cycles and are used to correlate important geological phenomena like marine anoxia, hydrothermal activity, regional tectonics and early-oxygenation events (Condie, 2001). Clays with their layered structure, possess negative charge, adsorb organic molecules in the interlayer sites, are very suitable in the geological environment for the growth and diversification of microbiota during the hydration-dehydration conditions (Maurel and Leclerc, 2016). According to Wachtershauser (1988), geochemistry is connected to biochemistry through the iron and sulphur prebiotic processes at low redox potential and formation of organic molecules in which clays promoted the reaction.

The $\delta^{13}\text{C}_{\text{org}}$ of the carbonaceous phyllites from the Chitradurga (-38.5 ‰ to -21.6 ‰ VPDB), Gadag (-24.3 ‰ to -14.67 ‰ VPDB), Sandur (-29.2 ‰ to -24.8 ‰ VPDB) and Shimoga greenstone belts (-24.6 ‰ to -11.8 ‰ VPDB) collectively reflect on organic carbon signatures (Sindhuja, 2021). This is supported by a recent study in the variably metamorphosed BIFs covering Paleoproterozoic to Paleoproterozoic with their biogenic signatures has important implications for the timing of the life's emergence on Earth. The BIFs associated with the Sandur carbonaceous shales gave $\delta^{13}\text{C}_{\text{org}}$ values of -28.5 ‰, supporting their biogenic nature (Dodd et al., 2019).

The detrital zircons from the carbonaceous phyllites of Chitradurga and Gadag (2476 ± 42 to 3254 ± 25 Ma), Sandur (2306 ± 28 to 2733 ± 31 Ma) and the Shimoga belt (2199 ± 24 to 3194 ± 18 Ma) suggest Meso to Neoproterozoic provenance (Sindhuja, 2021). The detrital zircon ages of stromatolitic carbonates and the carbonaceous phyllites collectively indicate the initiation of stromatolitic growth at 3.5 Ga and the organic matter started reaching the deeper part of the ocean basin ~ 3.3 Ga which continued up to Paleoproterozoic time and resulted in the deposition of carbonaceous shales (Fig. 1C).

Hydrogen sulphide released from the Archean Mid Oceanic ridge (AMOR) play an important role in stabilizing carbon compounds (Gonzalo et al., 2020) which is evidenced by sulfurization of organic matter through chemical reaction between sulfidic water and organic matter in the anoxic ocean water. The $\delta^{34}\text{S}$ of Chitradurga and Gadag carbonaceous shales ranging from 1.8-2 ‰ and 1.3-2 ‰ respectively reflect on magmatic hydrothermal signatures (Sindhuja et al., 2020). Influence of biogeochemical processes in the transformation of Au grains in arid environment has been observed in the gold mines of Western Australia. Gold grains consist of clays and organic matter which are remnants of biofilms that are responsible in the transformation of Au grains and dispersion of gold giving rise to geochemical anomalies (Fairbrother et al., 2012). Therefore, in the euxinic conditions, gold and other sulphides which have chemical

affinity with the Fe and carbon gets deposited within the sulphide facies BIFs, cherts and carbonaceous shales at the deep ocean conditions.

Conclusions

Based on the stratigraphic association in the field, trace element and isotopic characteristics of the BIFs, Mn formations, stromatolitic carbonates and carbonaceous phyllites, it is evident that the Archean Dharwar Ocean was characterized by anoxic to euxinic redox conditions. The volcano-exhalative activity at the AMOR provided Fe-Mn and Si rich solutions which created metal rich environment. Stromatolitic growth was initiated ~3.5 Ga at the continental shelf and generated O₂. Mn from the hydrothermal solutions of AMOR reached up to the shallow shelf as Mn needs relatively more O₂ than Fe, got precipitated. Ferrous reached to a relatively deeper shelf and got precipitated as BIFs due to the intermittent supply of iron and silica at the fluctuating thermal/chemical and acidic/alkaline conditions of Archean Oceans. The organic matter from the stromatolitic carbonates, detrital continental and within basin volcanic material reached to the ocean floor, degraded the organic matter and deposited as carbonaceous shales. Gold was deposited along the faults/folds and shear zones due to tectonic activity which is present within the sulphidic BIFs and carbonaceous shales. Therefore, the Chitradurga, Shimoga and Sandur greenstone belts preserved the Archean biogeochemical processes which transformed the toxic environment to a habitable Earth and enriched with Fe-Mn and gold deposits.

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Figure Caption:

Fig. 1: (A) and (B): Simplified geological map of Dharwar Craon with an Inset map showing different cratons of India. (C) Relative global abundance curve for Precambrian BIF along with calculated curves for the atmospheric evolution of oxygen and carbon dioxide from Klein(2005). The Neoproterozoic peak of BIF and Mn formations, 3.5-2.6 Ga stromatolitic growth and 3.3-2.1 Ga carbonaceous shales of Dharwar Craton are also indicated.

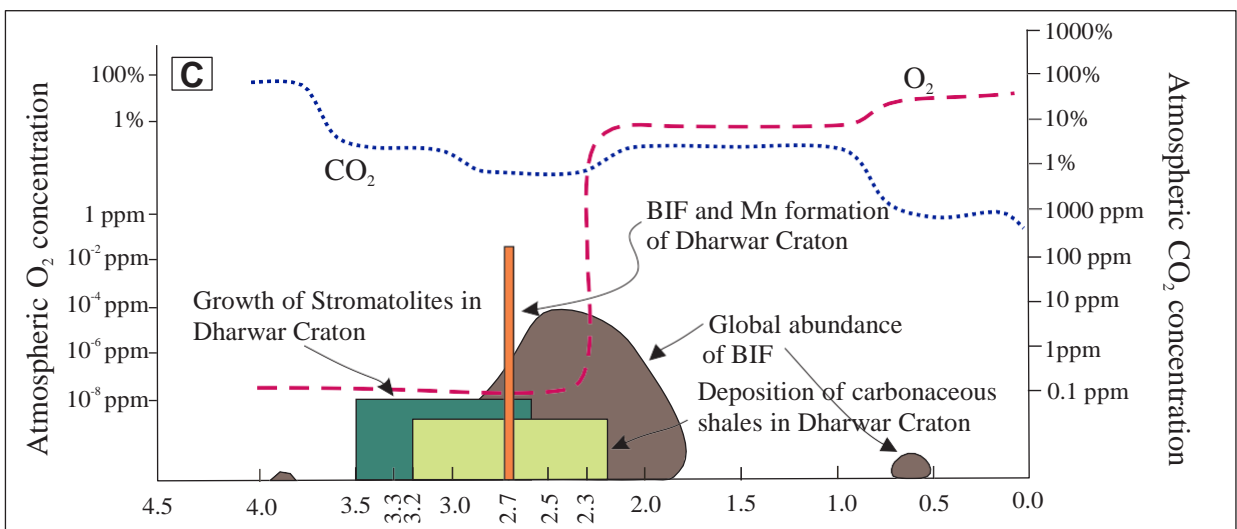
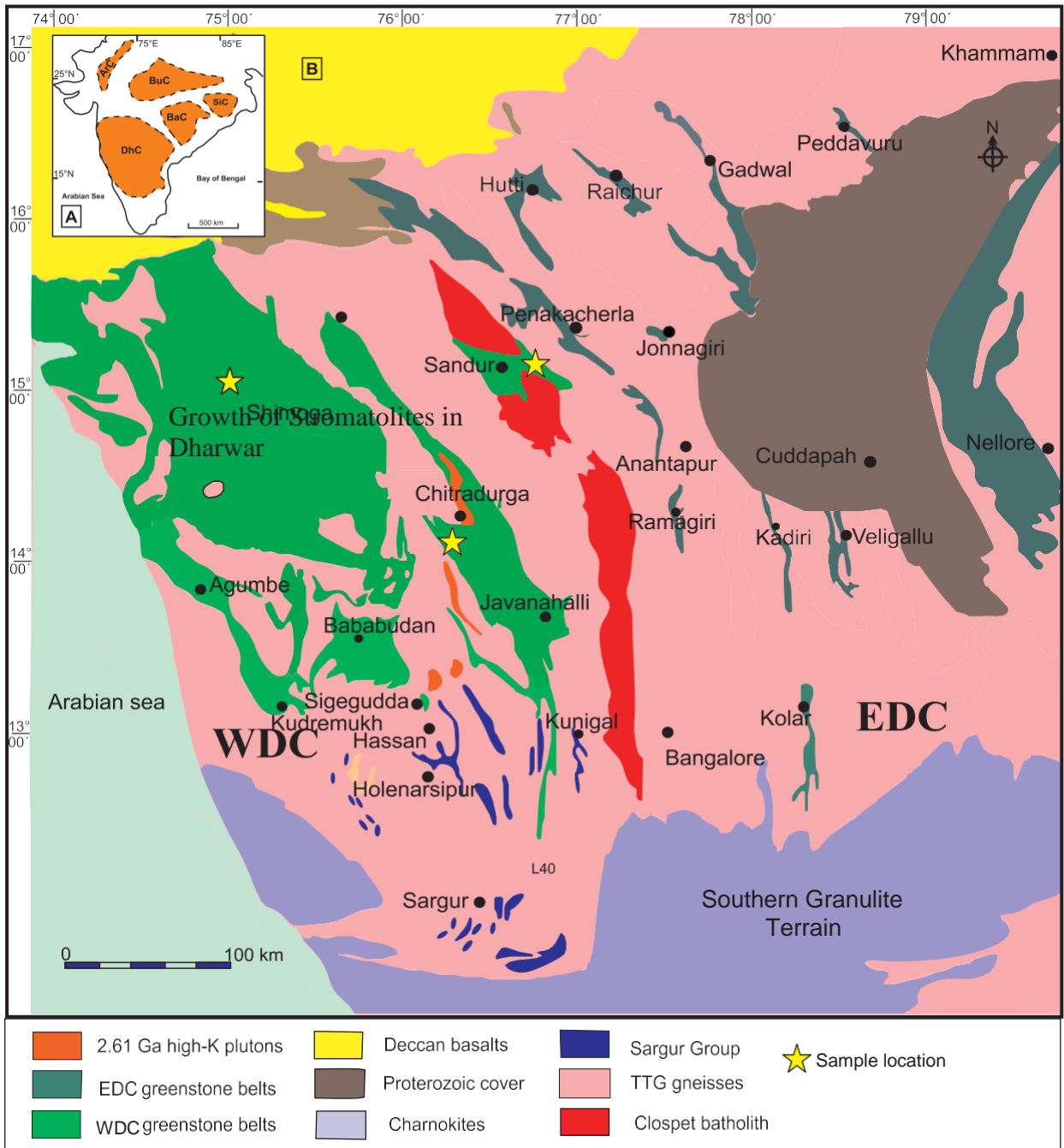


Fig 1