

Carbon isotope systematics of graphites from Dharwar craton, southern India: Implications to their source and post-depositional alterations

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Carbon isotope compositions of graphites present within carbonate-free diverse rocks of different metamorphic grades from the Dharwar and Sargur supracrustals show that their source is biogenic. No overall correlation is observed between grade of metamorphism and ^{13}C compositions. Extremely ^{13}C -depleted graphites from Kolar area point towards involvement of bacteria of methane cycle. Their wide range of ^{13}C values, however, is the result of changing chemical and thermal parameters of the gold-bearing mineralizing solution of Kolar. Large variation in isotopic ratios of Sargur graphites is predominantly due to initial isotopic heterogeneity of organic precursors, although graphites from the contact zone between ultramafic rock and pelitic schist are isotopically enriched due to metamorphism.

GRAPHITIC matter within rocks originates from three sources: (i) progressive dehydrogenation of organic matter during metamorphism of sedimentary rocks¹, (ii) a magmatic source, where precipitation of graphite takes place due to carbon-rich fluids that infiltrate low f_{O_2} rocks², and (iii) graphites originating from mineral reactions with carbonates³. In order to understand the origin of graphitic matter present within the Archean supracrustals of southern India and also to evaluate the effects of post-depositional alterations in the form of diagenesis, metamorphism and exchange with carbon-bearing fluids, we have undertaken carbon isotopic study on graphites from carbonate-free diverse rocks of different metamorphic grades. In this report we present our data and discuss their significance in relation to the source, the depositional environment and later alteration processes.

The > 2.5 Ga Archean rocks of the Dharwar craton have been divided into supracrustals of Sargur Group and Dharwar Supergroup⁴. The Dharwar Supergroup comprises of lower Bababudan and upper Chitradurga Groups. The NNW–SSE trending supracrustal belts of the Dharwar craton are metamorphosed in such a way that the greenschist facies rocks are exposed in the north, amphibolite in the middle and granulite facies

rocks in the south⁵. The Sargur supracrustals are metamorphosed to amphibolite/granulite facies and have been assigned an older sequence by some workers⁶, although others have opined that they represent higher grade metamorphic equivalents of the Dharwar supracrustals⁷. The auriferous belts of Dharwar craton have been named as a separate group, the Kolar Group, and are considered to be part of Dharwar Supergroup⁴. The graphites analysed in the present study are from Sargur supracrustals (Sargur Group) and Dharwar supracrustals (Bababudan, Chitradurga and Kolar Groups). The geological map⁸ along with sample locations and metamorphic isograds⁹ are shown in Figure 1.

The petrographic description of graphite-bearing rocks along with their mineral assemblages are given in Table 1. Graphites of Dharwar supracrustals are mainly associated with schist, metachert and phyllites^{10,11} while those of Sargur supracrustals with amphibolites, pelitic schists/gneisses, meta-ultramafites and quartzites^{12,13}. The graphites are both crystalline (flaky/platy) and/or amorphous (fine grained) in nature.

The graphitic material from Madanmaduvu and Nagavand areas of Chitradurga Group occurs respectively within fine-grained chloritic schist and graphitic schist with metachert. At Ingaldhal graphites are associated with sulphide facies banded iron formation and metachert. The graphitic carbon content of Chitradurga Group samples varies from < 1% (Madanmaduvu and Ingaldhal) to 3.5 wt% (Nagavand). Amorphous graphite occurs within phyllites of Chickmagalur–Kemangundi areas of Bababudan Group. These phyllites consist of fine-grained mica, quartz and iron ore. They are penetrated by lenses and veins of white quartz, on the edges of which graphite concentration has been noticed. The amount of graphitic carbon in the Bababudan phyllites is around 2 wt%. The Ganacharpura, Kolar Gold Field and Volagamadi areas of Kolar Group have graphite associated with fine-grained graphitic schist, metachert and gold-bearing quartz veins. The graphitic carbon content of Kolar Group samples varies from 5 to 10 wt%. The schistose rocks of Itna–Toravalli are amphibolites while Chikdevibetta, Sargur, Kalsargur and Hampapura areas of Sargur Group are kyanite–graphite schists and pelitic schist containing 2 to 5 wt% of flaky graphite. Platy graphites are also seen in the quartz veins which cut through the schists. In Mavinhalli area, ultrabasic dyke intrudes into the ultramafic pelitic gneiss and is graphitized on the margin. The content of graphite lies between 5 and 10 wt%. Graphites from Chikbanavar, Arjunbettahalli and Gollahalli occur as micaceous-looking spangle within white quartzites and fine-grained quartz veins. Approximate content of graphite in these rocks is 0.5 wt%. At Holavanhalli, graphite occurs in quartzite and associated fractured quartz veins, in the form of thin flakes. The average content of graphite is less than 1 wt%.

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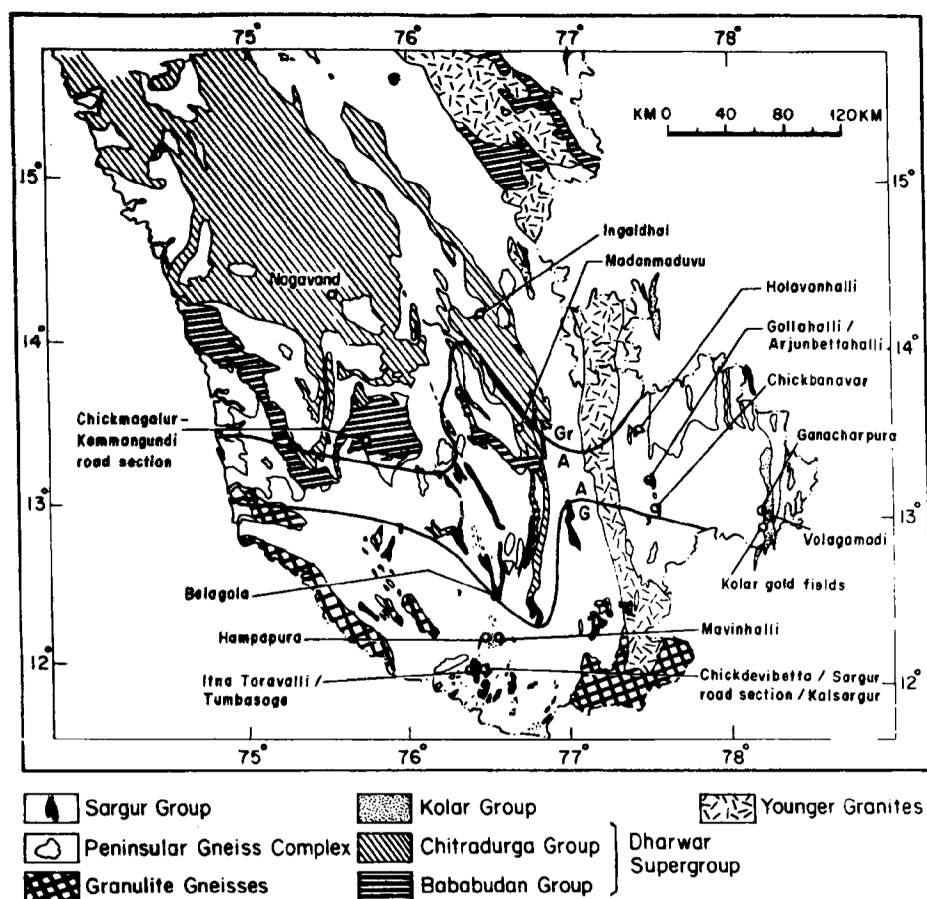


Figure 1. Geological map of part of the Dharwar craton (modified after ref. 8) showing locations of graphite bearing samples. Lines Gr/A and A/G are metamorphic isograds between greenschist–amphibolite and amphibolite–granulite respectively (after Raase *et al.*⁹).

The graphite-bearing rocks were crushed to ~120 mesh and each rock powder was treated with HF and HCl in a teflon beaker. The beaker was heated slowly to <100°C to dissolve silicates. The residue was repeatedly rinsed with double distilled water and dried in an oven. In some cases where graphite was present in the form of flakes or veinlets, it was carefully taken out and clean separates were handpicked under a binocular microscope. Purified graphitic fractions were degassed at 200°C under vacuum ($\sim 10^{-5}$ Torr) and reacted with excess V_2O_5 at 900°C. The resulting CO_2 was cleaned in the vacuum line and isotopic measurements were carried out using a VG 602 mass spectrometer. During the course of analyses, NBS-21 gave $-28.2 \pm 0.1\%$ (PDB).

Thirty-one graphite samples were analysed for their carbon isotopic compositions, 16 from the Sargur supracrustals and 15 from the Dharwar supracrustals (Table 1). Of the 15 graphites belonging to the Dharwar supracrustals, 5 are from Bababudan and Chitradurga Groups and remaining 10 are from Kolar Group. The number of samples analysed from Bababudan and Chitradurga Groups although small ($n = 5$), give useful

insight about their source. In that they show restricted range of ^{13}C compositions (-25.8 to -31.5% PDB) and fall within the 'normal' range of biogenic carbon ($\delta^{13}C = -25 \pm 6\%$ PDB) recorded in unmetamorphosed Precambrian rocks¹⁴. Most of the Kolar graphites are depleted in ^{13}C compared to the Bababudan and Chitradurga Groups and they exhibit remarkably large spread in ^{13}C values for any single location (see Table 1). Here 4 samples are from gold mine horizons, and the others are associated with sulphide, magnetite and quartz. Geological and mineralogical association indicate close relationship between the Kolar graphites and the ore-forming fluids of the Kolar Gold Fields. The ^{13}C values of these graphites were therefore controlled by chemical and thermal parameters of the mineralizing solution. Re–Os, Rb–Sr and O isotopic compositions determined on six different rock types of Kolar schist belt suggest large-scale fluid movement¹⁵. The fluids contained radiogenic Sr, highly radiogenic Os with $^{187}Os/^{186}Os$ (2.4 Ga) > 39 and heavier oxygen. It was proposed that the fluids probably acquired their radiogenic isotopic signatures from ancient crustal materials

Table 1. Sample location, rock type, mineralogical association and isotopic composition of graphite

Sample number	Location	Rock type	Major minerals	$\delta^{13}\text{C}$ (‰ PDB)
Dharwar supracrustals				
<i>(Chitradurga Group)</i>				
1.	Ingaldhal	Metachert with graphitic schist	Qtz, Ch, Mt	-31.5
2.	Madanmaduvu	Chloritic schist	Ch, Op	-29.0
3.	Nagavand	Chert with graphitic schist	Qtz, Hm	-25.8
<i>(Babubudan Group)</i>				
4.	Chikmagalur-Kemmangundi	Phyllite	Qtz, Ser	-28.2
5.	Chikmagalur-Kemmangundi	Phyllite	Qtz, Ser	-28.7
<i>(Kolar Group)</i>				
6.	Ganacharpura	Metachert with graphitic schist	Qtz, Mt	-37.1
7.	Ganacharpura	Metachert with graphitic schist	Qtz, Mt	-36.5
8.	Ganacharpura	Metachert with graphitic schist	Qtz, Mt	-36.3
9.	Ganacharpura	Metachert with graphitic schist	Qtz, Mt	-40.8
10.	Ganacharpura (drill core, 102.9 ft)	Metachert with graphitic schist	Qtz, Mt, Ser	-34.2
11.	Kolar Gold Fields (east of 89 Winze)	Metachert with graphitic schist	Qtz, Mt	-33.2
12.	Kolar Gold Fields (Nandidurg mines)	Metachert with graphitic schist	Qtz, Mt	-33.6
13.	Kolar Gold Fields	Metachert with graphitic schist	Qtz, Mt	-29.6
14.	Kolar Gold Fields	Metachert with graphitic schist	Qtz, Mt	-29.4
15.	Volagamadi	Metachert with graphitic schist	Qtz, Ser	-32.4
Sargur supracrustals				
16.	Itna Toravalli	Amphibolite	Amph, Mt, Qtz	-23.1
17.	Tumbasoge	Pelitic gneisses	Qtz, Sill	-29.0
18.	Chikdevibetta	Pelitic gneisses	Qtz, Kya, Stau	-24.3
19.	Chikdevibetta	Pelitic gneisses	Qtz, Kya, Ga	-22.0
20.	Sargur-Road section	Amphibolite	Amph, Py, Qtz	-36.3
21.	Kalsargur	Amphibolite	Amph, Py, Qtz	-34.8
22.	Hampapura	Pelitic schist	Kya, Qtz, Mt, Mu	-33.8
23.	Hampapura	Pelitic gneisses	Qtz, Kya, Stau	-30.7
24.	Mavinhalli	Ultramafic-Pelitic schist	Amph, Kya	-16.1
25.	Mavinhalli	Ultramafic-Pelitic schist	Amph, Kya	-17.6
26.	Gollahalli	Quartzite	Qtz	-19.4
27.	Arjunbettahalli	Quartzite	Qtz	-19.6
28.	Chikbanavar	Quartzite	Qtz, Bio	-18.7
29.	Chikbanavar	Quartzite	Qtz, Bio	-17.2
30.	Holavanhalli	Quartzite	Qtz, Amph, Ep	-19.5
31.	Belagola	Quartzite	Qtz, Bio	-15.7

Mineral abbreviations: Qtz, Quartz; Ser, Sericite; Ch, Chlorite; Mt, Magnetite; Op, Opaques; Hm, Hematite; Amph, Amphibole; Sill, Sillimanite; Kya, Kyanite; Stau, Staurolite; Ga, Garnet; Py, Pyroxene; Mu, Muscovite; Bio, Biotite; Ep, Epidote.

with long-term high $^{187}\text{Re}/^{186}\text{Os}$ (ref. 15). Maximum concentration of carbon (up to 10 wt%) in Ganacharpura suggests that the fluids were rich in carbon. Such fluids can result in wide variations in ^{13}C compositions of graphites depending upon the total concentration of carbon, fugacity of oxygen, pH of the solution and the temperature¹⁶. Similar large range of carbon isotopic composition has been recorded for the Late Archean gold-uranium conglomerates of the Witwatersrand System of South Africa¹⁷. The anomalously light ^{13}C values of graphites from Kolar area probably indicate that bacteria of the methane cycle (methanogens and methy-

lotrophs) were involved in the formation of the precursor organic matter¹⁸.

The Sargur Group of graphites exhibit large variations in their ^{13}C compositions (Table 1), although the precursors for graphites seem to be organic in origin. Those associated with pelitic schists, gneisses and amphibolites are mostly characterized by normal biogenic carbon and are depleted compared to the ones associated with quartzites and ultramafic-pelitic contact. Two processes can be considered to account for ^{13}C enrichment (i) metamorphism, and, (ii) initial carbon isotope heterogeneity of the organic carbon. Metamorphism causes posi-

tive shift in ^{13}C compositions of residual carbon due to preferential removal of ^{12}C as has been reported for sedimentary amorphous organic matter that was converted to graphite due to intrusion of massive Duluth gabbro within the sediments of Biwabik Formation up to a zone extending nearly 3 km from the contact¹⁹. Similarly, carbonaceous matters in a metamorphic profile from the Swiss Alps exhibit a positive shift in ^{13}C compositions up to about 14‰ (ref. 20). Samples from Mavinhalli (nos. 24 and 25) which come from the contact zone between ultramafic rock and pelitic schist, might have been enriched in ^{13}C compositions due to metamorphic activity associated with intrusion of ultramafic rock. However, such an interpretation for the other ^{13}C enriched-graphites of Sargur Group may not be valid. It is important to note that all the Sargur Group of graphites experienced thermal metamorphism up to a temperature of about 550–600°C (ref. 9). Hence the positive shifts observed in case of graphites associated with quartzites being caused due to metamorphic activity alone is not possible, although minor variations due to metamorphism cannot be ruled out. Furthermore, it has been pointed out that a large positive shift of about 10‰ is not inherent to the process of graphitization²¹. It is interesting to note that carbonaceous matter associated with the cherts of the Hamersley basin of western Australia exhibit ^{13}C compositions of about $-17.5 \pm 3.5\text{‰}$ (ref. 22) and are comparable to the values obtained by us. The Hamersley BIFs have not been affected at all by thermal metamorphism and oxygen isotopic study on coexisting mineral phases yield a temperature of diagenesis to be $< 300^\circ\text{C}$ (refs 23, 24). We therefore interpret that the carbon isotope variation of Sargur graphite has been predominantly caused due to initial variation of isotopic composition of the organic matter during pathways of carbon fixation associated with biological activity. This inference assumes significance in the light of experimental^{25,26} as well as theoretical²⁷ estimates of magnitude of $\delta^{13}\text{C}$ shift of kerogen (about 2‰) in response to post-depositional secondary fractionation accompanying carbon loss.

The present C-isotopic study on graphites of the Dharwar and Sargur supracrustals of southern India reveals that (a) the precursors of graphite appear to be biogenic in origin, (b) while the isotopic signatures of Sargur Group graphites from the contact zone between ultramafic rock and pelitic schist have altered significantly due to metamorphism, the others have retained their initial heterogeneous isotopic signatures and (c) extreme ^{13}C -depleted compositions of the Kolar Group of graphites probably indicate that bacteria of methane cycle represent the precursor for them. Their widely-variable $\delta^{13}\text{C}$ values, however, are resulted from

changing physico-chemical parameters of the gold-bearing mineralizing solutions of the Kolar Gold Fields.

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