PETROGRAPHY AND STABLE ISOTOPE GEOCHEMISTRY OF GRAPHITE BEARING COARSE GRAINED CALCITIC MARBLE:

A CASE STUDY FROM PARTS OF EASTERN GHATS PROVINCE

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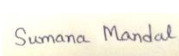

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Abstract

The calcitic marble rock in Araku vally of Eastern Ghats province is poly-metamorphosed and poly-deformed associated with metapelites have suffered granulite facies metamorphism. The stable assemblage of forsterite + spinel + calcite represent peak metamorphic condition. Graphite are present mainly on white coloured band of cakcitic marble rock. Graphite is present at the boundary of calcite, apatite, biotite and along the fracture of olivine and spinel. Textural study indictes formation of graphite after the formation of calcite and silicates. Graphite grains show deformational structure. Carbon isotope thermometry has been applied to coexisting calcite and graphite in calcitic marble rock. $\Delta^{13}C$ (Cc-Gr) is useful to estimate the temperature of formation of graphite from mathematical formula. Obtained temperature from the formula ranges between 855ºC to 952ºC. Carbon isotope ratio of a fluid deposited graphite is an important tool for identify the source of carbon (organic matter, mantle, or carbonates). $\delta^{13}C$ value for our sample ranges betwenn(-0.7—1.2) which indicate an inorganic carbon source. $\delta^{13}C$ and $\delta^{18}O$ value of calcite is also an important tool to indicate the source of carbon. Precipitation on graphite can occure from a CO_2 bearing fluid form due to decarbonation reaction at the prodrade path. From this fluid graphite can be precipited by cooling in retrograde path under low fO_2 condition.

CHAPTER 1

INTRODUCTION

CHAPTER 1: INTRODUCTION

1.1 INTRODUCTION

Eastern Ghats Mobile Belt is a high grade granulite terrain of utter geological interest. Enormous granulite exposures of high to ultra-high temperature have been studied for reconstruction of petrotectonic evolution of the belt. Thermal and tectonic history of exhumation of these granulitic rocks of granitic (granite, charnockite, enderbite, leptynite etc.), pelitic and calcitic marble variety in this proterozoic terrane (Karmakar et al., 2009, Karmakar & Fukuoka 1998, Das et al., 2011, Sengupta et al.1990, 1991, 1999, Dasgupta et al 1995, Bose et al. 2000, 2006, 2009, 2011) have been studied. There are some calcitic marble rocks also present in this area metamorphosed up to granulite facies.

In this study, a detailed petrographic, isotopic and thermometric investigation have been done for graphite bearing coarse grained marble. In EGMB, graphite is hosted within different types of rocks, which had been subjected to several episodes of metamorphism and deformation. Petrographic study gives an idea about the relative time of graphite formation with respect to the host rock mineralogy and deformation event. Carbon isotope study of graphite has been carried out to elucidate the origin of graphite from biogenic or abiogenic source. Isotopic composition of calcite-graphite pair has been used to deduce the peak temperature of metamorphism when calcite and graphite were in isotopic equilibrium.

1.2 REGIONAL GEOLOGY

The Eastern Ghats Mobile Belt(EGMB), a high grade granulite terrain, situated along the east coast of India as a linear disposition for over 900 Km and comprises an area of about 50,000 sq Km. The average width of the belt is 100 km which varies from 300 Km at the northern part to 20 Km at the southern part. The belt is geographically located approximately between 15N to 21N latitude and 80E to 86E longitude. Granulite facies metamorphism through the length and width of the belt, a prolonged history of mountain building spanning most of the Proterozoic era and orogenic activity continuing at least up to the Pan-African (cu. 500 Ma) (Karmakar et al. 2009, Mukhopadhyay et al. 2009). The cratons are of Archaean age and are composed of tonalite-trondhjemite-granite gneiss hosting supracrustal belts (Mukhopadhyay t al (2009).

Status of Eastern Ghats Province (EGP)

The Eastern Ghats Belt (EGB) is bounded to the north by the Singhbhum craton and to the west by the Bastar craton, the Dharwar craton and the Nellore-Khammam Schist Belt (Fig no 1). To the south the EGB disappears into the Indian Ocean a little south of Ongole in Andhra Pradesh. The EGMB is split into two segments by the Godavari Rift north of Ongole. It is also dissected by the Mahanadi Rift near the northern margin. The western boundary of the Eastern Ghats mobile belt (EGMB) against the Bastar Craton is an intrusive contact and more or less linear with a NNE-SSW trend. The northern boundary against the Singhbhum Craton is rather complex, and a host of granitoids separate the two geologic provinces of the EGMB and the Singhbhum Craton proposed a boundary thrust, and later workers considered a faulted boundary on the evidence of crushed rocks and blasto mylonites near this boundary. The NE-SW Eastern Ghats trend is rotated to WNW-ESE near this boundary. Also, the NW-SE

Singhbhum trend is rotated to N-S near the boundary. Over a large part of the Eastern Ghats the strike is NE-SW which slightly veers to N-S and NNW-SSE near the southern extremity.

Ramakrishnan et al. (1998) subdivided the EGMB longitudinally into four zones based on dominant lithological assemblages. From west to east the zones are as follows-

1. Western Charnockite Zone (WCZ) - This zone consists of charnockites, enderbites, basic granulites and minor enclaves of metasedimentary migmatites.

2. Western Khondalite Zone (WKZ) – It is comprised of a sequence of garnet-sillimanite-alkali feldspar gneisses with intercalations of quartzites, calcitic marble rocks and high-Mg-Al granulites. The metasedimentary sequence has been intruded by enderbite and charnockite plutons, and several massif-type anorthosite complexes.

3. Central Migmatite Zone (CMZ) - An intensely migmatized association of supracrustal granulites intruded by voluminous porphyritic granitoids and massif-type anorthosite is reported from this area.

4. Eastern Khondalite Zone (EKZ) – This zone strongly resembles with Western Khondalite Zone but devoid of any anorthosite bodies.

Chetty and his coworkers (Chetty, 2001; Chetty et al. 2003; and the references therein) subdivided the EGMB into several structural domains based on satellite imageries of identified mega lineaments and interpreted them as shear zones. The zones are as follows-

1. Sileru Shear Zone (SSZ) – It demarcates the eastern boundary of the WCZ.

2. Nagavalli-Vamasadhara Shear Zone (VSZ) - This major lineament trends NNW-SSE and divides the EGB into eastern and western blocks.

3. Mahanadi Shear Zone (MSZ) – The trend of this zone is nearly E-W separating the Northern most part of the EGB from the rest of the belt.

Rickers et al. (2001a) identified different domains based on Nd model ages combined with Rb-Sr and Pb isotopic data and divided EGMB into following four units (fig 1.2.1) :

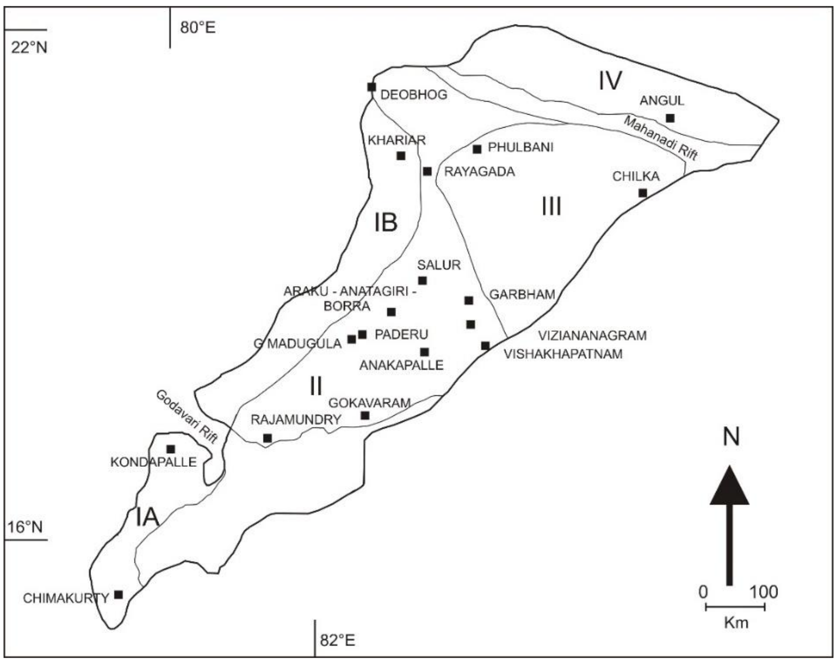


Fig-1.2.1: Domains based on isotopic data in the Eastern Ghats Belt (*after* Rickers et al. 2001a). Araku is in Domain II

Domain 1: It coincides with WCZ and consists of two sub- domains

1. Domain 1A: This domain lies to the south of the Godavari Rift. It is characterized by homogeneous Nd model ages. For the orthogneisses, the crustal residence times ranges from 2.3 to 2.5 Ga and for the paragneisses from 2.6 to 2.8 Ga. The age of the metamorphism is between 1.6 and 1.7 Ga. Source of the metasediments were the Archaean granitoid and greenstone materials.

2. Domain 1B: In the part of the WCZ north of the Godavari Rift the Nd model ages of enderbitic orthogneisses range from 3.2-3.9 Ga. Preliminary U-Pb data from zoned zircon grains indicate a high-grade metamorphic event at ~2.8 Ga, and the Pb isotopic data show no evidence of 1.6-1.7 Ga high grade event recorded in the Domain1A.

Domain 2: This domain is situated in between two shear zones, Sileru shear zone in the west and Nagavalli-Vamasadhara in the east. Nd model ages of the metasediments are homogeneous, around 2.1-2.5 Ga whereas for orthogneisses model ages are highly variable, around 1.8 - 3.2 Ga. The Sm -Nd and Pb isotopic data are consistent with the model of reworking of inhomogeneous Archaean crust during later granulite facies metamorphism, with variable input of juvenile material. Domain 2 has more Archaean components.

Domain 3: This domain represents reworked homogeneous early Proterozoic material and is surrounded by the Nagavalli-Vamasadhara and the Mahanadi lineaments. Ages for both the orthogneisses and the metasediments is homogeneous, around 1.8 to 2.2 Ga. Domain 3 had more juvenile additions.

Rickers et al. (2001a) suggested that either the Domain 2 or 3 are totally unrelated blocks or Domain 3 represents a position away from the orogenic front and Domain 2 close to it.

Domain 4: It is in the north of Mahanadi Lineament. Nd model ages are 2.2-2.8 Ga for meta-sediments and 3.2 Ga for orthogneisses, which is similar to the model ages from the

Depending on individual geological history, Dobmeier and Raith (2003) presented a classification of the EGB into four provinces. The provinces are subdivided into a total of 12 domains, each being characterized by specific lithology, structure and metamorphic grade. The four provinces are (fig 1.2.2):

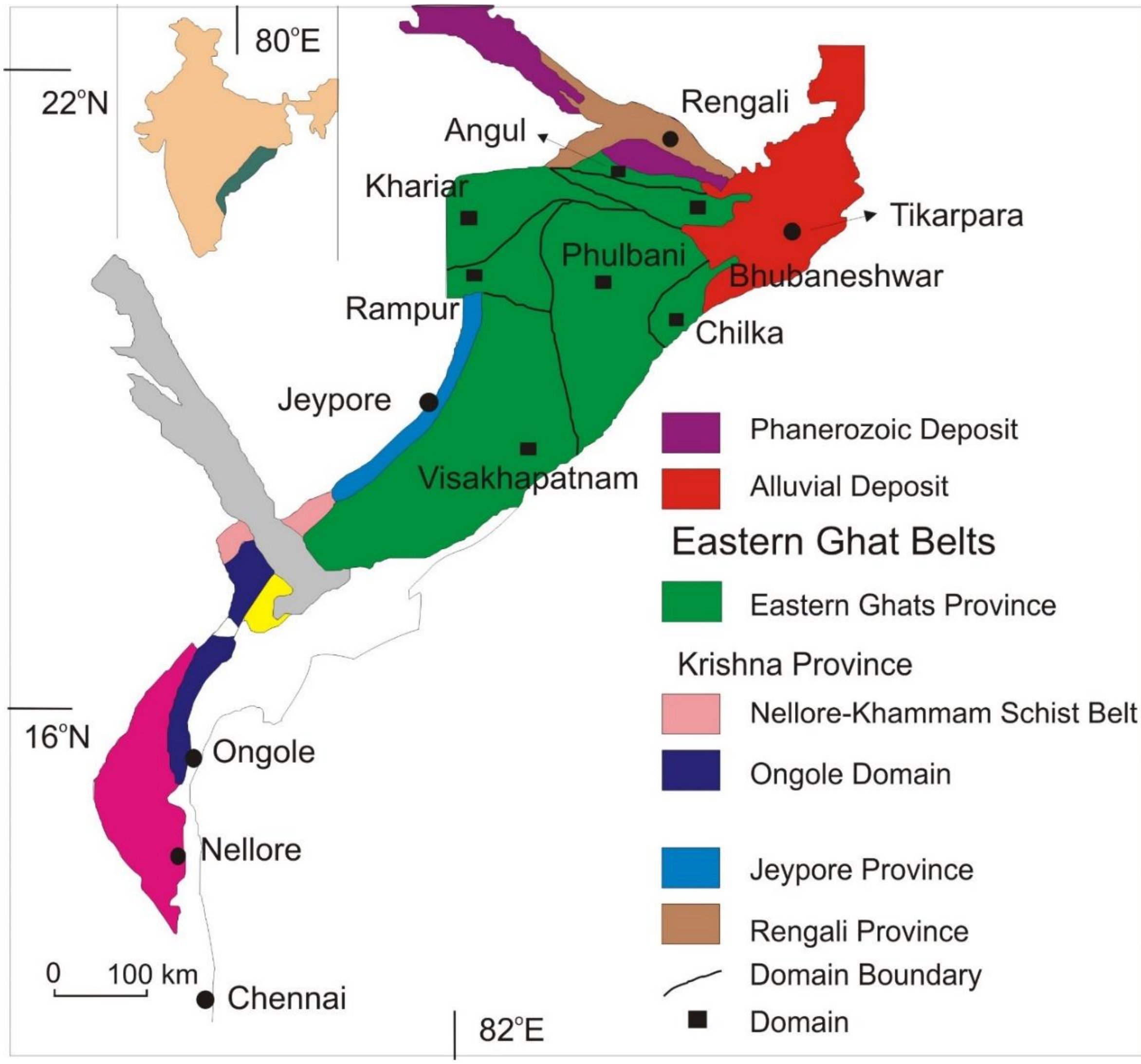


Fig 1.2.2: Provinces and domains of the Eastern Ghat mobile belt classified by Dobmeier and Raith (2003).

Jeypore Province (JP):

It has Bastar craton as its western periphery .The WCZ and the TZ north of the Godavari Rift, i.e., the Domain 1B of Rickers et al. (2001a) falls under Jeypore Province. The rocks found in this province are charnockite-enderbite, mafic granulite, with minor pelitic gneiss.

Krishna Province (KP):

This includes the Ongole Domain and the low- to medium grade Nellore-Khammam Schist Belt. The former is equivalent to southern part of WCZ or Domain 1A of Rickers et al. 2001a and the latter is equivalent to Udayagiri Domain and Vinjamuru Domain. In the Ongole Domain the dominant rocks are mafic granulite and large bodies of enderbitic gneiss and leptynite. The diatexitic metapelitic granulite containing profuse garnetiferous quartzofeldspathic leucosomes, high-Mg-Al granulite, quartzite and calcitic marble gneiss with metasedimentary rocks occurring as rafts within them. The metasedimentary rocks are intruded by layered mafic-ultramafic complexes, which are themselves invaded by the enderbite. The Udayagiri Domain and the Vinjamuru Domain are in greenschist and amphibolite facies respectively.

Eastern Ghats Province (EGP):

This comprises the major part of EGB and includes the WKZ, the CMZ and the EKZ, i.e., the Domains 2, 3 and part of 4 of Rickers et al. (2001a). The principal rock types are diatexitic pelitic gneiss (khondalite), high-Mg-Al granulite, calcitic marble gneiss, mafic granulite and enderbite, interspersed with massif-type anorthosite and intrusive granite-charnockite complexes. It is subdivided into seven domains, out of which are the Phulbani and the Visakhapatnam Domains (on either side of the Nagavalli-Vamasadhara mega lineament) are the biggest.

Rengali Province (RP):

This is the northernmost province of the EGB and is fragmented into several fault bounded blocks. The regional trend of foliation is WNW-ESE. The rocks are low to medium grade volcano-sedimentary sequences assigned to the Singhbhum craton (Mahalik 1994) and medium to high grade orthogneisses assigned to the Eastern Ghats Belt (Mahalik 1994). There was extensive felsic magmatism at~2.8 Ga. Nash et al. (1996) and Fachmann (2001) assigned the assemblage north of the Kerajang Fault to the Singhbhum Craton while the gneisses to the south were assigned to the Eastern Ghats Belt. Crow et al. (2001, 2003) suggested that an amphibolite facies assemblage, which extends south of the Kerajang Fault up to the Eastern Ghats Boundary Fault shows similarity to the package of the Rengali Domain, and on the other hand to the north of the Kerajang Fault a block of granulite facies rocks occurs. Rengali province is excluded from the Eastern Ghats belt as seen from the overall character of the province.

Geology of Eastern Ghats Province

The Eastern Ghats Province comprises of the vast terrain surrounding Vishakhapatnam as classified by Rickers et al. (2001). This domain extends from the Sileru Shear Zone in the west, Nagavalli – Vamasadhara Shear Zone in the north-northwest to the Godavari Rift in the south. North of the Godavari Rift also an early UHT (~1000°C) metamorphic event (M1) at crustal depths of 30-35km (8-10 kb) is reported from high-Mg-Al granulites in several areas like Anantagiri (Sengupta et al. 1990), Anakapalle (Dasgupta et al. 1994; Rickers et al. 2001b; Sanyal and Fukuoka, 1995), Araku (Sengupta et al. 1991, Karmakar & Fukuoka 1992, 1998). Prograde path of M1 metamorphism could not be reconstructed everywhere. Dasgupta and Sengupta (2003, and the references therein) said that the prograde path is under a fluid absent or deficient condition. Break down of biotite produce spinel+cordierite and cordierite+garnet assemblages in restite. The Peak metarorphic condition is 8-10 kb pressure and ~1000°C T. In peak metamorphic condition cordierite breakdown stabilize sapphirine+quartz and spinel+quartz assemblage. Shaw and Arima (1996a, 1996b) argued that the peak P-T condition was 12 kb and 1100°C for rock of Raydaga. Using Al thermometry for clinopyroxene the obtained peak metamorphic T is 950°-1020°C.

After reaching the peak condition the rock start to follow a retrograde path with decompression and moderate cooling. The UHT metamorphic assemblage is not present everywhere but the geochronological data support that this whole province has suffered UHT metamorphism. In cooling path the produced mineral assemblage is orthopyroxene+sillimanite+garnet in high Mg Al granulite. According to several workers (Dasgupta and Sengupta, 2003; Dasgupta et al. 1992, 1995; Dobmeier and Raith, 2003; Rickers et al. 2001b; Sengupta et al. 1990, 1999; Karmakar & Fukuoka 1998, Simmat and Raith, 2008) this granulite has suffered a M_2 metamorphism. The peak condition of M_2 is 8-8.5 kb and 800°-850°C. In between M1 and M_2 enderbite-charnockite intruded in supracrustal rock. The retrograde path of M2 is characterized by near isothermal cooling and decompression to ~5 kb.

1.3 STUDY AREA

Araku valley is situated in the NW of Vishakhapatnam city in Andhra Pradesh and is close to Orissa state border. The place is located on the Vishakhapatnam - Kirondal branch line, 119 km away from Vishakhapatnam and 85kms from Koraput. It comprises an area of 115 km. The valley is approximately in between 17^{o}24' N to 18^{o}33'N latitudes and 78^{o}24'E to 82^{o}55'E longitude. It is situated in the **Central Migmatitic Zone (CMZ)** according to Ramakrishnan et al. (1998) and according to Rickers et al. (2001a); the area is located within the **Domain 2**. According to Dobmeier and Raith (2003), the area is situated in **Eastern Ghats Province.**

The study area is situated at approximately 20km south-east of Araku valley at 18°10.477'N latitude and 82°55.814'E longitude.

1.4 OBJECTIVE OF THE PRESENT STUDY

1) Petrography of the graphite bearing marble

2) Mineral chemistry of the phases present in the rock

3) Stable isotope study (carbon and oxygen) from graphite and calcite

4) Estimation of temperature of formation of graphite and source of carbon in graphite

CHAPTER 2

FIELD RELATION AND PETROGRAPHY

CHAPTER 2: FIELD RELATION AND PETROGRAPHY

2.1 FIELD RELATION

The studied rock represents a thick banded unit consisting of white coloured band and a grey coloured band (Fig no 2.1.a). The white coloured band comprises big calcite crystals of pegmatitic appearance. This layer has isolated crystals of brown coloured mica, mob coloured spinel and blue coloured apatite visible under naked eye. Thin disseminated needles as well as coarse flakes of graphite are present within this pegmatoidal calcitic marble rock (Fig no 2.1.b). The graphite flakes are concentrated in places and form irregular small patches. The grey band is comparatively rich in silicate minerals than associated pure white coloured calcitic layer. High abundance of brown coloured mica is noticed in both the layers. The cluster of graphite is rare in the silicate rich part while disseminated fine graphite needles are ubiquitous. The concentration of graphite is modally high in the white marble layer characterized by the appearance of pegmatoidal carbonate phases. In the following sections the white pegmatoidal marble layer is characterized by petrography, mineral chemistry and stable isotope study.

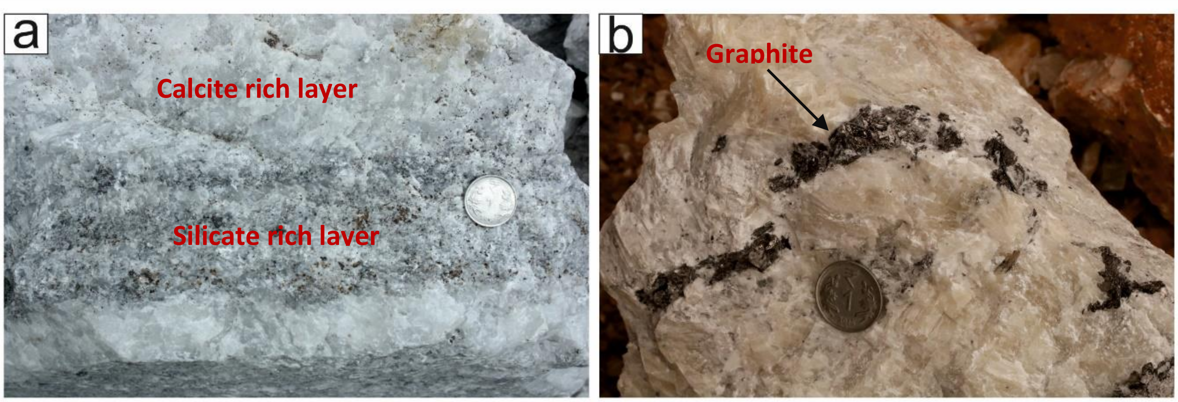


Fig 2.1: (a) Band of silicate rich layer in coarse calcitic pegmatoidal carbonate rock
(b) Occurrence of graphite within calcitic carbonate

2.2 PETROGRAPHY

2.2. A Mineral Identification

The studied coarse white coloured marble layer is characterized by the mineral assemblage comprising calcite, dolomite, biotite, olivine, spinel, apatite and opaque.

There are two type of opaque grains viz.

i) Elongated oriented graphite

ii) Anhedral non oriented opaque

The above mentioned minerals are identified by the following distinguishing optical properties under transmitted light microscopy:

Calcite: under plane polarized light it is colourless. Two set of cleavage is prominent (out of three set). It shows twinkling effect and fourth order interference colour. .

Biotite: Typically yellowish, brownish green or reddish brown, and distinctly pleochroic with parallel extinction. Birefringence is strong and yields variegated interference colours in the range of second to third order Sometime the interference colour is masked by the strong body colour.

Olivine: under plane polarized light it is colourless and highly fractured with high relief. No cleavage present. Under cross polarized light it shows second order blue interference colour.

Spinel: Colourless in thin section under plane polars and there is no cleavage plane present. It is isotropic and remains in extinction position under cross polarized light.

Apatite: under plane polarized light it is colourless and rounded to sub-rounded shape. Under cross polarized light it shows grey to first order blue interference colours.

Graphite: It is black under plane polarized light and elongated in nature. Under reflected light it shows yellowish colour.

2.2.B Textural Relationship

The studied rock is a banded pegmatoidal marble consisting of two prominent layers. (i) one layer (white in colour) is made up of predominantly calcite (more than 90% in volume) and dolomite with sparsely distributed olivine, spinel and apatite; (ii) another layer is grey coloured characterized by a greater proportion of silicate minerals including clinopyroxene, plagioclase, apatite with calcite and dolomite. Ubiquitous presence of biotite is common in both the domains. Graphite is present in both the layers but mainly concentrated in carbonate rich layer. The occurrence of graphite in carbonate layer is described here.

2.2.C Mode of occurrence of Graphite

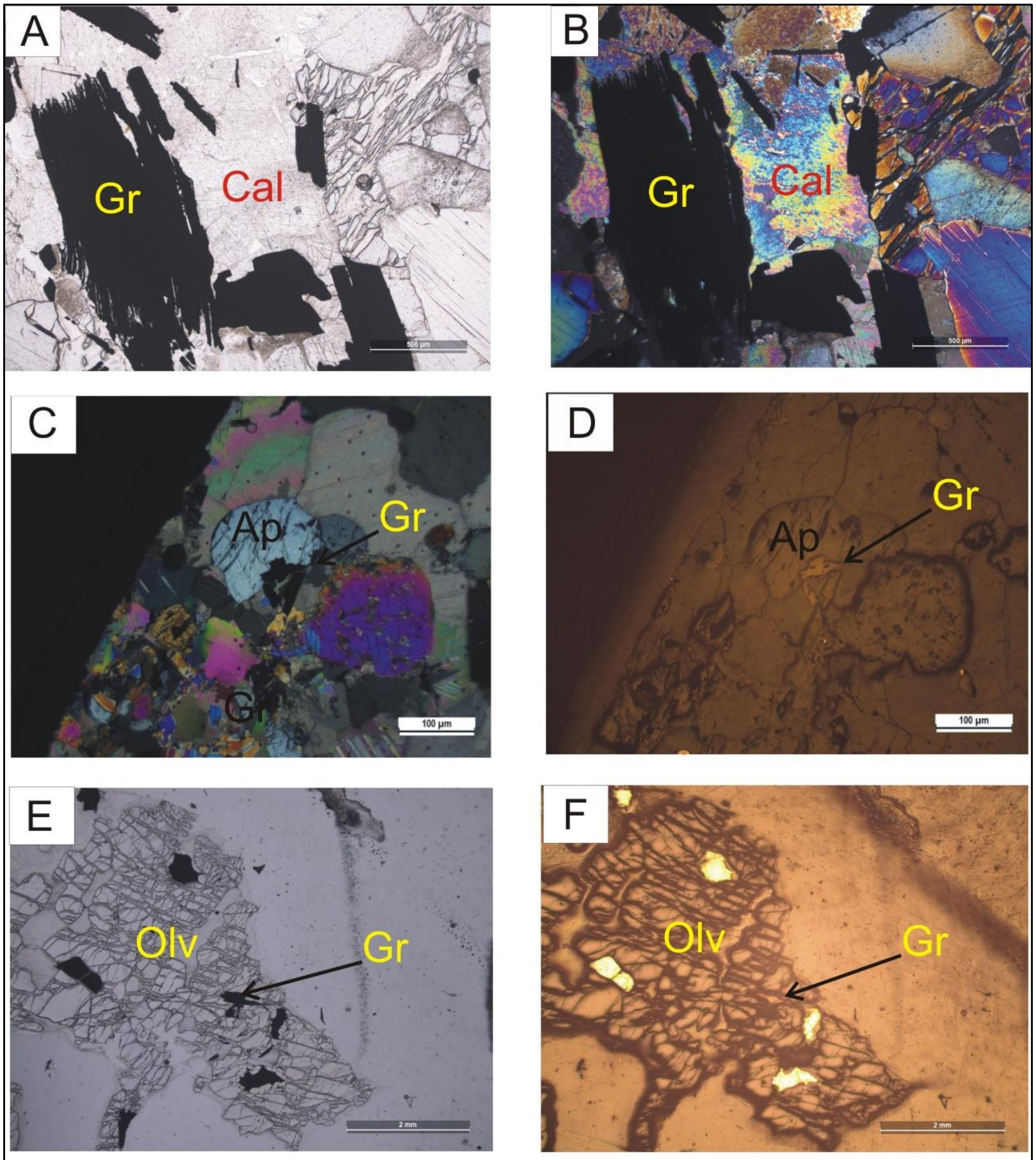
Graphite bearing carbonate layer consists largely of very coarse grained calcite and biotite with less frequently olivine, spinel and apatite.

Calcite is the main constituent matrix mineral in the studied rock. Calcite is coarse grained, subhedral and present as matrix in intergranular spaces of other minerals. Graphite occurs as disseminated grains within matrix calcite as well as along their boundaries. These disseminated graphite grains are coarse flakes and needles (Fig no 2.2.A). Graphite flakes measure 0.75 to 1.5 mm in length and consist of thin, micaceous foliation. Coalescence of diversely oriented and cross-cutting flakes and tablets of graphite often gives rise to masses of graphite in the matrix. This mass of graphite appears wedge shaped and massive tabular in some places.

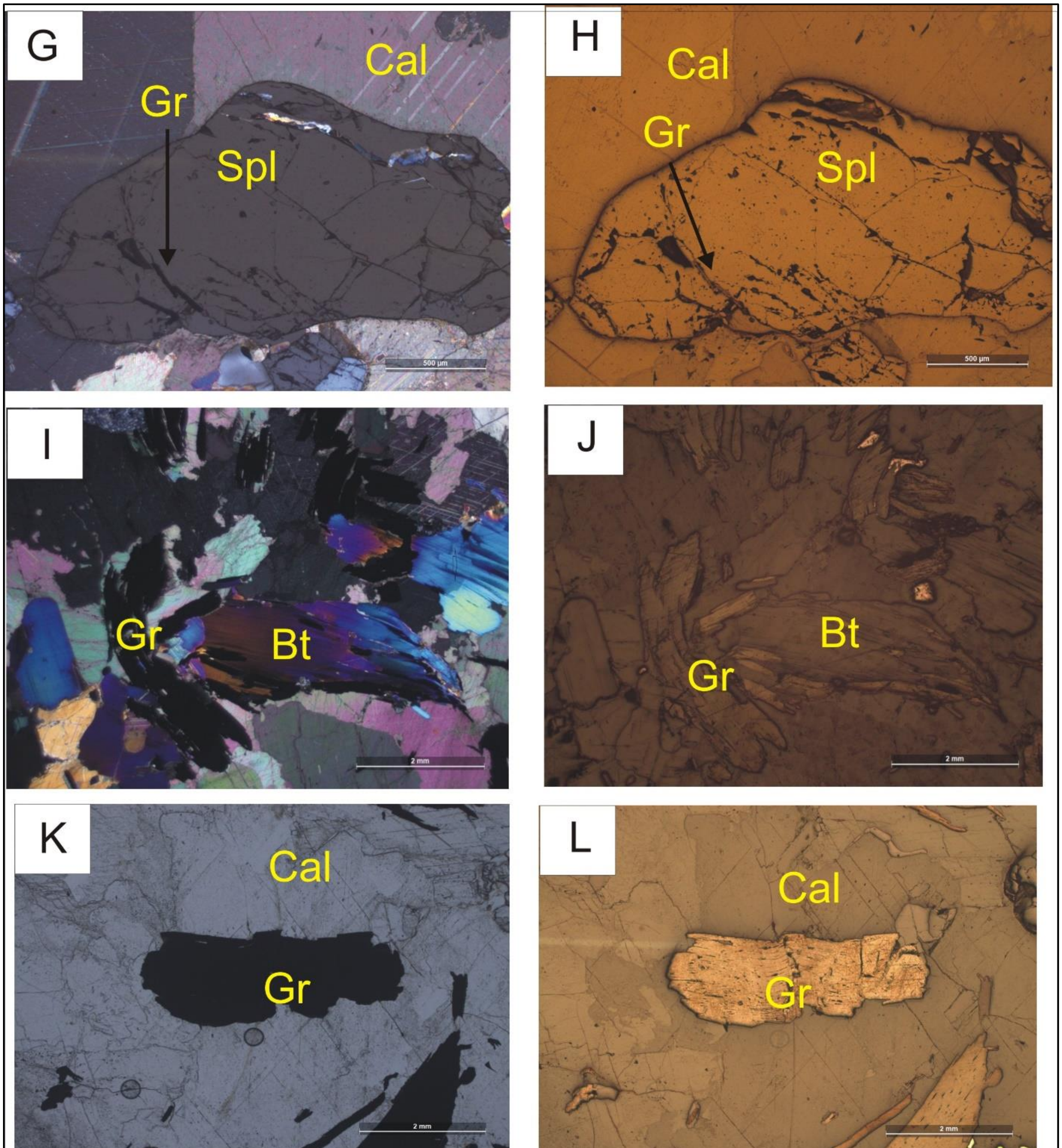
Sub-rounded to rounded apatite crystals are set in calcite matrix showing a distinct triple junction in some places. Elongated flakes or needles of graphite are attached to majority of the apatite crystals or sometimes partially enclosed. They occur mainly at the boundary and needles are intruded within the apatite grains along the boundary (Fig no 2.2.C and Fig no 2.2.D).They have no preferred orientation.

Olivine grains are highly fractured and fractures are filled by serpentine. Olivine grains have corrugated boundaries with calcite. Olivine grains have calcite and biotite inclusions. Commonly graphite flakes occupy grain boundaries of olivine or partially enclosed. Some of the fractures of olivine are filled by graphite and the orientation controlled by fractures (Fig no 2.2.E and Fig no 2.2.F). The flakes and needles associated with olivine is smaller in size.

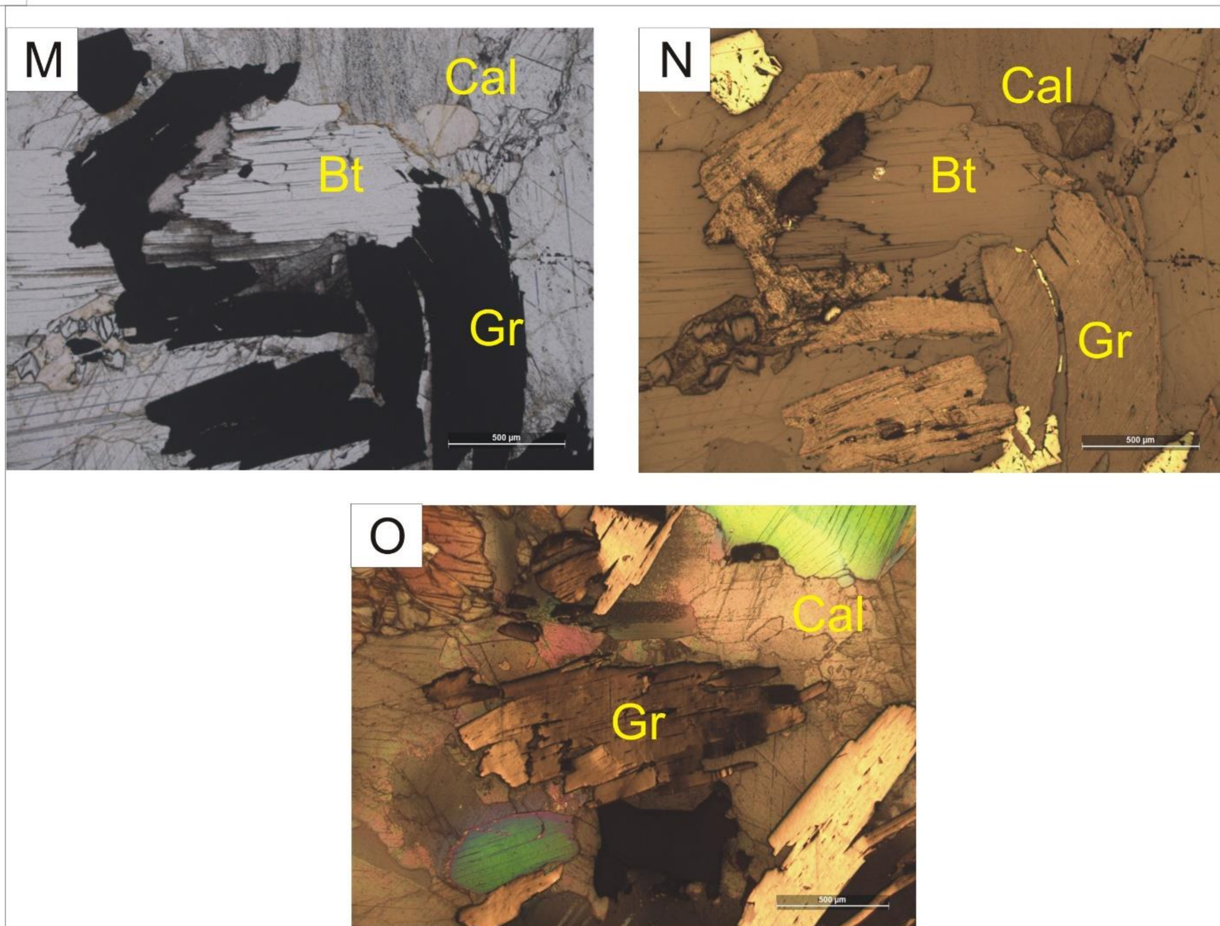
Fine flakes of graphite are also arranged parallel or sub-parallel to the boundaries of coarse grained spinel embedded in calcite matrix. These spinel grains shows equilibrium boundary relation with calcite. Here the graphite flakes are mainly fractured filled (Fig no 2.2.G and Fig no 2.3.H). Coarse biotite grains are intimately associated with matrix calcite. The elongated biotite grains show a foliation. The stringers of graphite are diversely oriented at margins of biotite grains. The cleavages of biotite are often penetrated by graphite needles with the orientation of cleavage plane (Fig no 2.2.I and Fig no 2.2.J). Masses of graphite are sometimes curved in places. At some places, these aggregates of graphite are warped against biotite margins (Fig no 2.2.I and Fig no 2.2.J). Locally diversely oriented graphite masses partially enclose biotite grains (Fig no 2.4.K and Fig no2.4.L). A conspicuous feature of thick tabular graphite found in reflected light is kinking with double or multiple hinges (Fig no 2.2.K) . They exhibit conjugate kink zones developed oblique to the cleavage. Graphite needles oriented parallel to the biotite margins bend to form a curvilinear boundary along with biotite. They often show protrusions from the grain margins inward in multiple directions. The graphite flakes as well as masses of graphite exhibit undulatory extinction in many places (Fig no 2.5.O).



2.2.A Graphite at the boundary of calcite under ppl
B. Graphite at the boundary of calcite under cpl
C. Graphite at the boundary of apatite under cpl
D. Graphite at the boundary of apatite under reflected light
E. Graphite along the gracture of olivine under ppl
F. Graphite along the fracture of olivine under reflected light



2.2. G. Graphite along the fracture of spinel under cpl
H. Graphite along the fracture of spinel under reflected light
I. Warping of graphite at the margin of biotite under cpl
J. Warping of graphite at the margin of biotite under reflected light
K. Kinked graphite within calcite matrix under ppl
L. Kinked graphite within calcite matrix under reflected light



2.2. M. Graphite rimming botite under ppl
N. Graphite rimming biotite under reflected light
O. Graphite showing undulatory extinction under reflected light

2.3 MINERAL CHEMISTRY

The mineral chemical oxide data has been provided by the supervisor only for the use of this unpublished M.Sc. dissertation. The mineral formula recalculation has been done using excel sheet. The salient phase chemical features of the minerals belonging to the white coloured band are described here.

CALCITE

Calcites in the rock is not pure calcite in composition. There is some amount of magnesium where Mg content varies from 0.912 to 0.919(a.p.f.u.)

BIOTITE

The composition of biotite is close to the phlogopite end member composition with high Mg no of 0.994 to 0.995 Al in phlogopite varies from 1.091 to 1.164. Biotite is Ti bearing where Ti ranges from 0.040 to 0.045.

OLIVINE

Olivine is nearly forsterite end member with Xmg varying from 0.982 to 0.986 Ca content is up to 0.000 to 0.004

APATITE

Apatite is F bearing with F content varying from with some insignificant amount of Cl.

SPINEL

Spinel is Mg rich with Xmg averaging 0.96. Zn is present with Zn varying from 0 to 0.004871 with little amount of Cr present.

2.4 EVOLUTION OF GRAPHITE BEARING ASSEMBLAGE:

The white coloured very coarse grained calcitic marble is the main host rock of graphite. The crystal plastic deformation referred in the textural studies suggests the rock is deformed and metamorphosed (Fig no 2.4.I and Fig no 2.4.N).The stable assemblage of forsterite + spinel + calcite indicates granulite facies condition where progressive stages of metamorphism are absent. Graphite is preferentially concentrated at grain margins of calcite, biotite, apatite, olivine and spinel. This occurrence of graphite suggests its formation after stabilization of the aforesaid minerals. The diverse orientation of graphite indicates absence of directed pressure during their formation. The cross cutting and coalescing graphite results from grain growth in several directions. Warped mass of graphite against biotite flakes is indicative of deformation event. Slip parallel to their length gives rise to warped tablets with step like outline. The conspicuous feature of graphite is kinking observed in reflected light. Kinking could have developed due to translation. Double hinge and multiple hinges are exhibited by the kinks. Conjugate kinks are defined by axial planes of the kinks oriented parallel or at angles to each other. The different limbs of kinks have contrasting reflection pleochroism resulting in heterogeneous tone and strong anisotropism. The development of kinking matches well the kinking exhibited by biotite. Graphite flakes frequently exhibit undulatory extinction interpreted to occur as a result of subsolidus deformation. Thus, deformation of graphite and juxtaposed biotite is indicated by the presence of kinking and warping.

CHAPTER 3

STABLE ISOTOPE GEOCHEMISTRY

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Stable isotopes are non-radioactive forms of atom (^{12}C, ^{13}C, ^{16}O, ^{18}O). They show mass dependent fractionation. Fractionation of isotope between two compounds depends on their bond strength. Heavier isotopes prefer stronger bonds where lighter isotopes are preferentially fractionated into compounds with lighter bonds. . In case of carbon there are two stable isotopes ^{12}C and ^{13}C. Organic matter such as tree takes less ^{13}C and more ^{12}C during respiration. So if any mineral have organic source the ^{13}C value will be less and $\delta^{13}C$ value will be negative. On the other hand inorganic matter such as carbonates are ^{18}O rich as small highly charged atom, C4+ is bonded with O with a stronger bond. Stable isotopes are helpful in two important ways. It can be used as geochemical tracer. The isotopic ratio of element or rocks can elucidate the source of element as well as the different processes the elements have gone through. Secondly the isotopic ratio of two substances can be used as potential geothermometer if they are in equilibrium.

(Selected stable isotope data have been provided by the supervisor only for the use of this unpublished M.Sc. dissertation. Only the synthesis of the stable isotopic data has been presented here.)

3.1 DESCRIPTION OF STABLE ISOTOPE STUDY

Carbon and oxygen isotopes have been studied here. The graphite flakes are powdered and isotopic value of graphite has been measured. From the powdered grains of calcite immediately adjacent to graphite carbon and oxygen isotopic ratios are obtained. Using $\delta^{13}C$ values of coexisting calcite and graphite calculated Δ (Cc-Gr) has a direct relation with the temperature of formation of graphite. $\delta^{13}C$ and $\delta^{18}O$ values of the host calcite reflect the protolith of the host rock. Thus the results of the stable isotope study have been utilized to decipher the temperature of graphite formation and source of carbon in graphite.

3.2 RESULTS AND INTERPRETATION

3.2.A Temperature of formation of graphite:

Carbon isotope fractionation between two phases strongly depends on temperature (Sanyal et al., 2009). The fractionation of carbon isotope between calcite and graphite decreases as metamorphic grade increases (VALLEY and O'NEIL, 1981; Wada and SUZUKI, 1983; MORIKIYO, 1984). Therefore, small Δ (Cc-Gr) results from isotopic exchange at high temperature during metamorphism. The exchange of carbon **i**sotope is pressure independent so the thermometer is a pressure independent geothermometer. This is a sensitive thermometer for high grade calcitic marble rocks.

It is assumed that the carbon isotope ratio at peak metamorphism condition preserved by graphite. The carbon isotope value of graphite and calcite pairs thus indicate the peak temperature condition if calcite and graphite are in equilibrium (Scheele and Hoef 1992, Chacko et al. 2001). However, there is a small change in carbon isotope value due to isotopic exchange at retrograde path. Due to the slow rate of diffusion of carbon isotope in graphite (Thrower and Mayer, 1978) and the absence of third carbon bearing phase it acts like an ideal geothermometer. Value of Δ13C calcite-graphite decrease with increasing grade as a result of isotopic exchange and less fractionation.

By using the equation Δ13C calcite-graphite = δ13C calcite - δ13C graphite we got that the Δ13C calcite-graphite value is in between 3.8 to 4.8. This narrow range of Δ13C calcite-graphite value indicate that the sample have preserved isotopic equilibrium.

Now following the equation of Kitchen and Valley (1995);

$\Delta^{13}C$ (calcite-graphite) = 3.56* 10^6*T^{-2}

The equilibration temperature of calcite-graphite to be in the range of 840℃ to 940℃ that indicates high temperature to ultra-high temperature condition (fig no 2.1). This is the peak temperature of the equilibrium assemblage as calcite and graphite are in isotopic equilibrium.

Pressure of peak metamorphic condition could not be deduced due to absence of any suitable geobarometers.

According to the equation of Dunn and Valley (1992)

$\Delta^{13}C$ (calcite-graphite) = 5.81* 10^6*T^{-2}- 2.61

Estimated temperature ranges from 855℃ to 952℃, which is well consistent with the temperature range found using the equation of Kitchen and Valley (1995)

The Temperature against $\Delta^{13}C$ calcite-graphite plot suggests an equilibrium exchange between calcite and graphite.

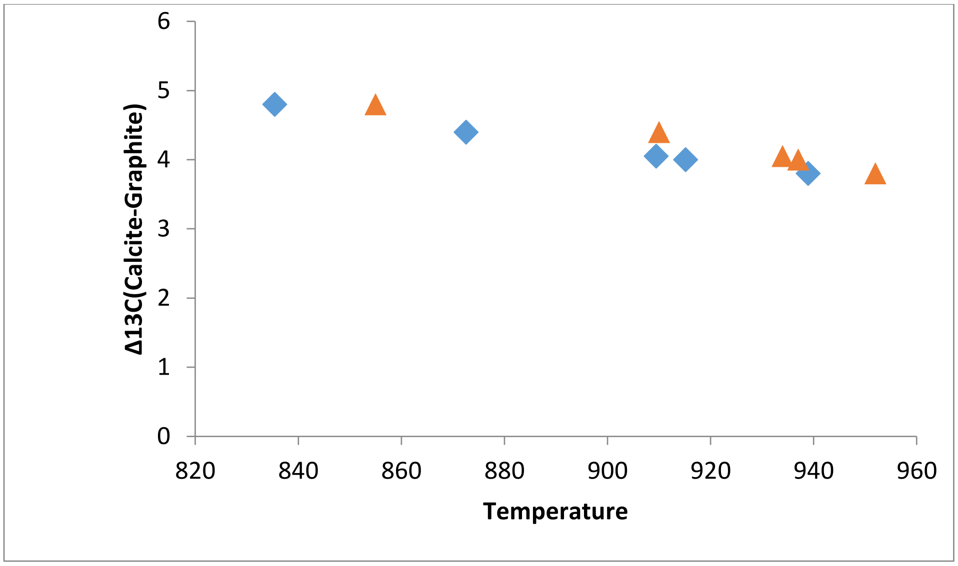
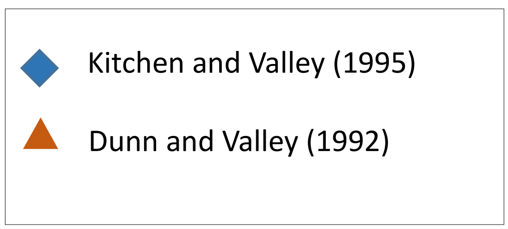


Fig no 3.1 Estimation of temperature of formation of graphite from $\Delta C_{Calcite–Graphite}$ geothermometer



3.2.B Origin of carbon in graphite from isotopic evidences:

Considerable debate has been focused on the origin of carbon in graphite deposits in granulites. Until the routine application of stable carbon isotope ratios to decipher the origin of carbon in graphite, arguments favouring the biogenic or abiogenic derivation of carbon were based on field data or on experimental chemistry and thermodynamic calculations in carbon systems. In view of diversity in graphite formation the source of graphite is important to understand the origin of graphite. In case of biogenic graphite the $\delta^{13}C$ value is very less (fig no 3.2). The average $\delta^{13}C$ value for organic matter is about −25‰. For non-biogenic graphite this value is much more. Inorganic limestone have higher $\delta^{13}C$ (−2‰ to 0‰). This is because the biogenic graphite is rich in ^{12}C but the abiogenic graphite has higher ^{13}C. The ratio of this two isotopes is represented by $\delta^{13}C$ which can indicate the source of carbon. The $\delta^{13}C$ value can be expressed by the formula

$$\delta^{13}C\ {}^{o}/_{oo} = \{ (^{13}c/^{12}c)_{graphite} / (^{13}c/^{12}c)_{standard} - 1\} * 1000$$

The graphite formation and $\delta^{13}C$ value of graphite have a wide range depending on the lithology of the rock, which are elaborately discussed below. It has been demonstrated using a chart below (fig no 3.2) for calcitic marble granulite rock this value range from -2.4‰ to 26.6‰ (Sharma et. al). For khondalite, this value range from (-16.6‰ to -24.6‰) and for pegmatite it is in between (8.8‰ to-26.6‰).The average $\delta^{13}C$ value for organic matter is about −25‰; inorganic limestone, on the other hand, have higher $\delta^{13}C$ (−2‰ to 0‰) value. This value is -7‰ for graphite from mantle derived fluid (Schidlowski).

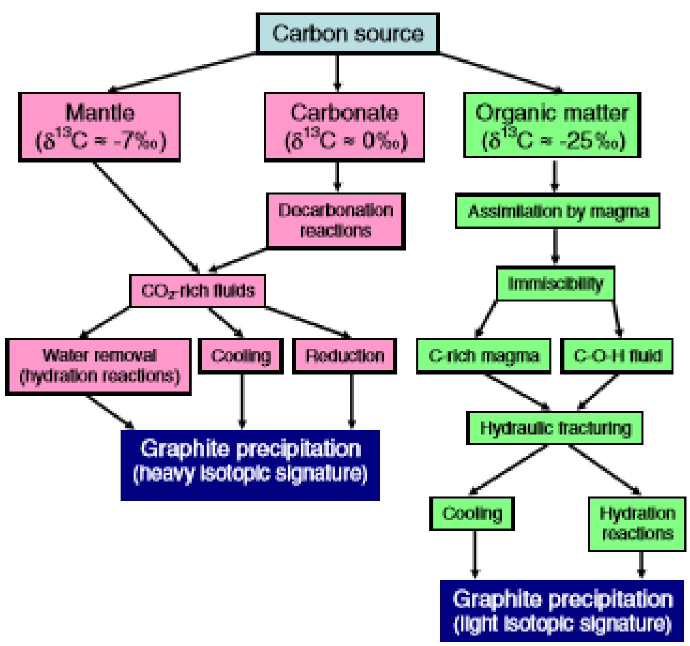


Fig no 3.2 Diagram summarizing the mechanisms involved in different graphite mineralization in granulite-facies rocks (Luque et al, 2014)

The $\delta^{13}C$ value in the studied samples ranges in between (-0.7 to -1.2per mil). Therefore, $\delta^{13}C$ value suggests an inorganic source of graphite in carbonate rocks. The $\delta^{18}O$ value of adjoining calcite is in between (-1.2 to 3.7 per mil). The $\delta^{13}C$ and $\delta^{18}O$ value of rock sample rule out any carbonatitic affinity and indicate that the environment was sedimentary with high degree of evaporation (Rothe and hoefs,1977) indicating a crustal source. The carbonate rock of this area preserved original isotopic composition and the large differences were caused by devolatilization reaction at high temperature. In case of calcitic marble granulite rock CO_2 produced by decarbonation reaction at prograde path can change the pristine character of carbonate through exchange. It indicate a crustal source.

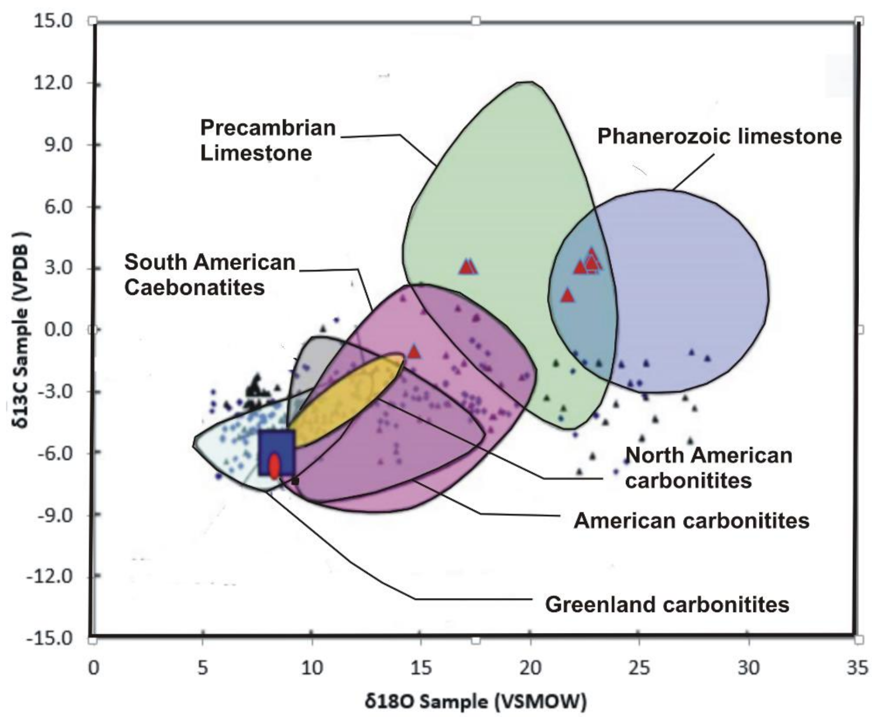


Fig no 3.3 host rock of carbon from $\delta^{13}C$ and $\delta^{18}O$ value of calcite in calcitic marble rock (Keith Bell.AntoniSo simonetti, 2009)

3.2.C Mechanisms of graphite deposition

Decarbonation of the present assemblage plays a key role in graphite formation The CO_2 liberated through decarbonation reactions during metamorphism will be enriched in $\delta^{13}C$ relative to the organic matter. This CO_2 could be reduced to form graphite under granulite facies conditions in low oxygen fugacity (Lamb and Valley, 1984).

The graphite deposition can be graphically represented by C-O-H ternary diagram (fig no 3.4). The stability field of graphite is a function of temperature, pressure, bulk composition and CO_2. At specified P and T, a certain fluid composition will be in equilibrium with graphite, those along the ‘graphite saturation curve’. The graphite stability field increases due to decrease in temperature and/or increase in pressure (Luque et al., 1998). From Fig 3.4, P2>P1, T2>T1; in both the conditions stability field of graphite increases leading to the formation of graphite. Low fO_2 condition and presence of reducing agents can also induce precipitation of graphite (Luque et al., 1998).

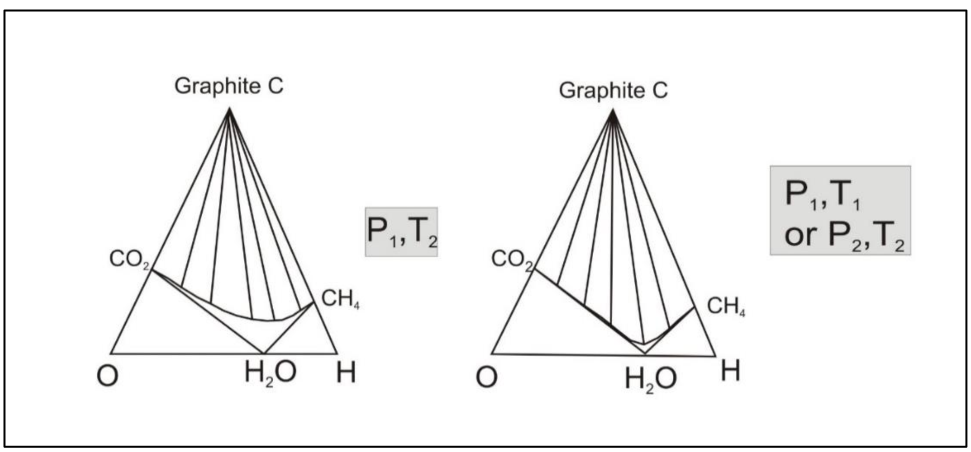


Fig no 3.4 C-O-H triangular diagram depicts the stability field of graphite as a function of temperature (T) and pressure (P) as shown by Ohmoto and Kerrick1977, Ferry and Baumgartner.1987. In figure, P2>P1 and T2>T1

CHAPTER 4

DISCUSSION AND CONCLUSION

CHAPTER 4: DISCUSSION AND CONCLUSION

The white coloured coarse-grained pegmatoidal marble consists of calcite, dolomite, biotite, spinel and apatite. Petrography reveals the rocks are recrystallized, deformed and metamosphosed. The $\Delta^{13}C$ value (calculated from the difference between $\delta^{13}C$ graphite and $\delta^{13}C$ calcite in equilibrium) is strongly temperature dependent. The estimated temperature from the pressure insensitive formulation from $\Delta^{13}C$ value suggests the graphite bearing equilibrium mineral assemblage in marble is metamorphosed up to high to ultrahigh temperature condition. However, pressure could not be estimated due to absence of suitable barometric equilibria $\delta^{13}C$ value in graphite (-1.2 to 3.7 $^{o}/_{oo}$) indicates inorganic carbon source for graphite in carbonate rocks. $\delta^{13}C$ in graphite and $\delta^{18}O$ in calcite rule out any possibility of carbonatite source. The CO_2 could be liberated from de-carbonation reactions occurring at prograde to peak condition of metamorphism of marble. The graphite could be precipitated from CO_2 in the marble rocks possibly during a cooling event in a low fO_2 condition.

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