PETROLOGY OF COARSE CALCITIC MARBLE FROM PARTS OF EASTERN GHATS PROVINCE, INDIA

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ABSTRACT

The coarse grained calcitic marble rocks from part of Eastern Ghats Province have been studied to decipher the petrological evolution. The white coloured calcitic marble consists of grey coloured band(s). The white coloured part (association (a)) is rich in carbonate phases containing abundant coarse calcite crystals and minor dolomite with biotite, olivine, spinel, amphibole, apatite, graphite and iron sulphide. The grey coloured band (association (b)) has modally higher abundance of silicate phases over carbonates. Association (b) contains calcite, biotite, clinopyroxene, plagioclase and apatite (± graphite). Overall granoblastic texture and crystal plastic deformation reveal that the rocks are deformed and metamorphosed. Calcite contains minor amount of Mg, which decreases from core to rim (X_{mg} = 0.002–0.06). Silicate phases are compositionally close to the Mg end member. Reaction textures and modelling in C-space suggest that Mg-bearing calcite + biotite ± silica developed the peak metamorphic assemblages of (i) forsterite, calcite, spinel and (ii) diopside, anorthite (+ calcite) respectively for association (a) and (b). Dolomite exsolution in Mg-bearing calcite and formation of secondary amphibole, biotite and serpentine after olive and pyroxene document the retrograde history of metamorphism. Solvus thermometry using reintegrated composition of exsolved dolomite and host calcite records peak metamorphic temperature above 850°C. However, matrix calcite composition estimates down temperature of ~500^{O}C, which suggests a retrograde cooling event. Peak pressure could not be estimated due to absence of any suitable geobarometry. Therefore, this study shows that the coarse grained marble rock suffered deformation – metamorphism in granulite facies condition above 850°C followed by a cooling event with drop in temperature of at least 350^{O}C.

CHAPTER 1

INTRODUCTION

Eastern Ghats Mobile Belt (EGMB), a polydeformed and polymetamorphosed terrain, exposes a deep crustal section containing varieties of metapelites, different types of granites and gneisses, charnockites, basic and intermediate rocks, anorthosites and alkaline igneous plutons (Naqvi and Rogers, 1987). Several studies from Eastern Ghats granulite belt suggests extreme temperature condition at 8-9 kbar pressure (Sengupta et al., 1990; Sengupta, Karmakar, Dasgupta and Fukuoka, 1991; Karmakar et al., 2009; Dasgupta et al., 1995) predominantly from the metapelites. In contrast to that high grade calc-silicate rocks in EGMB have been less attended to decipher the metamorphic evolution of the area. But calc-silicate including impure marbles, metamorphosed to granulite facies conditions provide important tools in constraining pressure-temperature fluid histories of high grade terrains (Warren et al, 1987; Motoyoshi et al., 1991; Harley & Buick 1992; Bucher-Nurminen, 1981).

In the present work a thick banded unit of extremely coarse calcitic marble comprising alternate carbonate-rich and silicate rich layers has been chosen to present detailed textural and phase compositional study. In addition, the exsolution texture of dolomite within the host calcite gives key information to estimate metamorphic temperature conditions. Calcite-dolomite solvus thermometry is applied here where the compositional re-integration between calcite and exsolved dolomite lamellae are used to determine the peak metamorphic temperature before exsolution (Anovitz & Essene, 1987; Puhan, 1979, Mizouchi et al., 2010). The composition of Mg-calcite after exsolution gives information about re-equilibrated temperature condition.

BACKGROUND GEOLOGY

Regional Geology

The Eastern Ghats Mobile Belt (EGMB) is a NE-SW trending arcuate Precambrian fold belt (Krishnan 1961) of high-grade granulite rocks extending along the east coast of India from north of Cuttack in Orissa to Nellore in Andhra Pradesh of India (R. S. Sharma, 2009). The linear disposition of the belt is over 900 Km and comprises an area of about 50,000 sq Km. The belt has a maximum width of 100 km in the northern part and less than 20 km in the south where it is concealed under the Phanerozoic cover. The fold belt is in contact with three cratonic blocks, namely the Singhbhum (-Orissa) craton in the north, the Bastar craton in the west, and the Dharwar craton in the south and southwest (Naqvi and Rogers 1987, Mukhopadhyay Basak (2009). To the east of the fold belt is the Bay of Bengal. The cratons are of Archaean age and are composed of tonalite-trondhjemite-granite gneiss hosting supracrustal belts. 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 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.

Available information on the geological and tectonic settings in different sectors and segments in EGMB suggest it to be a composite orogenic belt comprising several 'lithozones', 'provinces' or 'domains that are characterised by distinct geological histories and separated from each other by tectonic boundaries.

According to Bhattacharya (1996), the EGMB comprises two major rock groups: one charnockitic and the other khondalitic. The charnockitic group consists of mafic to acidic charnockites, hypersthene-bearing granulites, gneisses and leptynites while the khondalitic group includes garnetsillimanite gneisses, quartzites and calc-silicates. Based on the dominant lithological assemblages:

ZONAL CLASSIFICATION: Nanda and Pati (1989) and Ramakrishnan et al. (1998) proposed a 4-fold longitudinal division of the EGMB on the basis of dominant lithological assemblages from west to east.

- **Western Charnockite Zone (WCZ)**, dominantly shows charnockite and enderbite with lenses of mafic-ultramafic rocks and minor metapelites.
- **Western Khondalite Zone (WKZ)**, dominated by metapelite (khondalite) with intercalated quartzite, calc-silicate rocks, marble and high Mg−Al granulites. The metapelitic granulites are intruded by charnockite/ enderbite. Several occurrences of massif-type anorthosites are also reported from this zone (Bolangir, Turkel and Jugsaipatna).
- **Central Charnockite-Migmatite Zone (CMZ)** has dominantly migmatitic gneisses but also includes high Mg−Al granulites and calc-silicate rocks, all of which are intruded by charnockite-enderbite, pophyritic granitoids and massive-type anorthosite (Chilka Lake region)
- **Eastern Khondalite zone (EKZ)**, having lithological similarity with WKZ, but without anorthosite.

TERRANE CLASSIFICATION: Another classification of EGMB was proposed by Chetty (2001) based on the presence of shear zones, stretching lineation, different fold styles and axial planes of early formed folds. This structural classification is termed as Terrane Classification. It divides the EGMB into 9 distinct terranes that are merged along the shear zones and lineaments:

- **Godavari Terrane**
- **Koraput Terrane**
- **Viziamagaram Terrane**
- **Rayagada Terrane**
- **Berhampur Terrane**
- **Phulbani Terrane**
- **Angul Terrane**
- **Balangir Terrane**
- **Talcher Terrane**

  The major shear zones are **Sileru Shear Zone (SSZ),** marking the eastern boundary of the WCZ , **Nagavalli-Vamasadhara Shear Zone**, trending NNW-SSE divides the EGB into eastern and western blocks, **Mahanadi Shear Zone (MSZ)** in the north trending nearly E-W and separating the northernmost part of the EGB from the rest of the belt.

DOMAIN CLASSIFICATION : Rickers et al., (2001) carried out a systematic isotopic study over the belt to discriminate between juvenile and reworked crustal material. Based on Nd-model ages combined with Rb- Sr and Pb isotopic data they distinguished 4 domains (Fig. 1.2.1) which partly coincide with the lithozones of Ramakrishnan et al., (1998).

- **Domain 1:** This broadly coincides with the WCZ and is subdivided into two domains.

  Domain 1A: This domain lies to the south of the Godavari Rift and is characterized by homogeneous Nd model ages. The crustal residence times for the orthogneisses range 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. The metasediments were derived from a source containing Archaean granitoid and greenstone materials.

  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 Domain 1A.

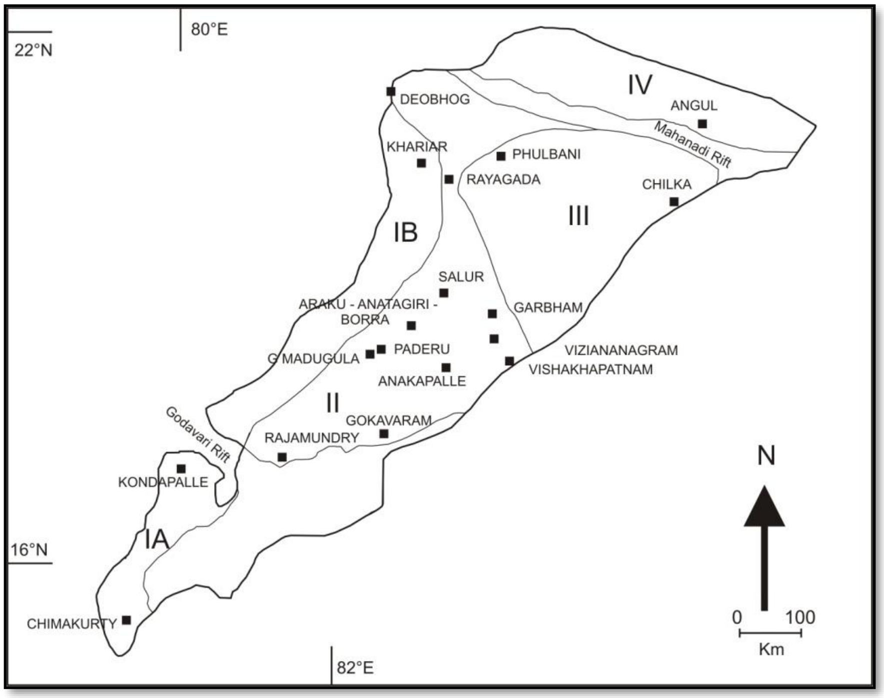

Fig 1.2.1: Domain Classification according to isotopic data by Rickers et al. (2001).

- **Domain 2:** This is bounded to the west by the Sileru Shear Zone (SSZ) and to the east by the Nagavalli- Vamasadhara lineament. The metasediments have rather homogeneous Nd model ages of 2.1-2.5 Ga. The orthogneisses have highly variable model ages of 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 3:** This is bounded by the Nagavalli- Vamasadhara lineament and the Mahanadi lineament and shows homogeneous Nd model ages of 1.8 to 2.2 Ga for both the orthogneisses and the metasediments. It is interpreted that this domain represents reworked (during Grenvillian orogeny), homogeneous early Proterozoic material. Domain 3 had more juvenile additions and Domain 2 had more Archaean components. Rickers et al. (2001a) opine that either the Domains 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:** In this domain lying to the north of the Mahanadi lineament the metasediments display Nd model ages of 2.2-2.8 Ga and the orthogneisses have Nd model ages of around 3.2 Ga, indistinguishable from the model ages from the Eastern Indian craton. It is to be noted that except for Domain 1 the other domains cut across the boundaries of the zones delineated by Ramakrishnan et al. (1998).

PROVINCE CLASSIFICATION: Dobmeir and Raith (2003) proposed a classification of EGMB and the adjoining regions of lower metamorphic grade into four 'Provinces' based on integrated structural, metamorphic and geochronologic information (Fig. 1.2.2). These are the (1) Jeypore, (2) Rengali, (3) Krishna and (4) Eastern Ghats Provinces. A 'Province'' was defined as a crustal segment with a distinct geological history.

- **Jeypore Province (JP):** Its western contact is with the Bastar craton, and it includes the WCZ and the TZ north of the Godavari Rift, i.e., the Domain 1B of Rickers et al. (2001a). The rocks are charnockite-enderbite, mafic granulite, with minor pelitic gneiss.

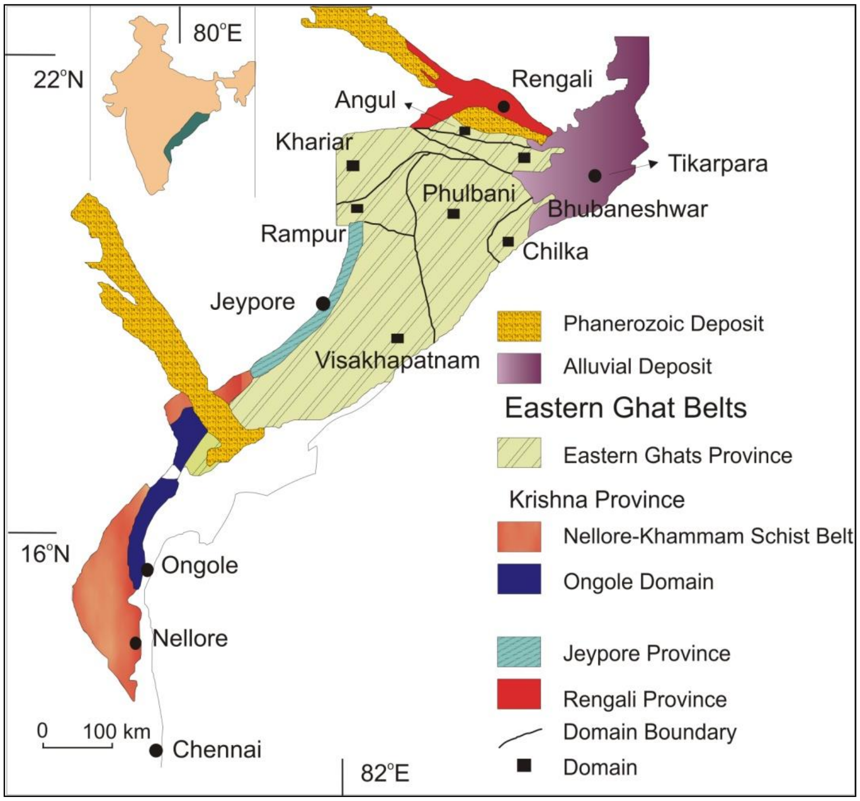

Fig 1.2.2 : Provinces and domains of the Eastern Ghat mobile belt classified by Dobmeier and Raith (2003).

- **Krishna Province (KP):** This includes the Ongole Domain (equivalent to southern part of WCZ or Domain 1A of Rickers et al. 2001a), and the low- to medium-grade Nellore-

Khammam Schist Belt (Udayagiri Domain and Vinjamuru Domain). In the Ongole Domain the dominant rocks are mafic granulite and large bodies of enderbitic gneiss and leptynite. The metasedimentary rocks occurring as rafts within the meta-igneous rocks are stromatic to diatexitic metapelitic granulite containing profuse garnetiferous quartzofeldspathic leucosomes, high-Mg-Al granulite, quartzite and calc-silicate gneiss. Layered mafic-ultramafic complexes, such as the one at Kondapalle, intrude the metasedimentary rocks and are themselves invaded by the enderbite. The other two domains of this province, the Udayagiri Domain and the Vinjamuru Domain, are in greenschist and amphibolite facies metamorphic states respectively, but the inclusion of these within the EGB is questionable.

- **Eastern Ghats Province (EGP):** This constitutes the major part of EGMB and includes the WKZ, the CMZ and the EKZ, i.e., the Domains 2, 3 and part of 4 of Rickers et al. (2001). The principal rock types are diatexitic pelitic gneiss (khondalite), small bodies of high-Mg-Al granulite, calcsilicate gneiss, mafic granulite and enderbite, interspersed with massif-type anorthosite and intrusive granitecharnockite complexes. It is subdivided into seven domains, the biggest of which are the Phulbani and the Visakhapatnam Domains on either side of the Nagavalli Vamasadhara megalineament.
- **Rengali Province (RP):** This is the northernmost province of the EGB. It is fragmented into several fault bounded blocks and the regional trend of foliation is WNW-ESE. The rocks are low to medium grade volcanosedimentary sequences and medium to high grade orthogneisses. There was extensive felsic magmatism at ~2.8 Ga. Mahalik (1994) assigned the high grade gneiss assemblages to the Eastern Ghats Belt and the low to medium grade supracrustal sequences to the Singhbhum craton.

Geological Evolution of Eastern Ghats Province

“Eastern Ghats Province” is a singular tern which comprises a large part of Domain 2 and parts of Domain 3 (Chilka, Phulbani, Angul and other blocks).

The history of Domain 2 was presumably initiated with the formation of a basin by a thermal pulse within the basement during ca. 1.76–1.70 Ga (Bose et al. (2011) based on zircon inherited age signatures). A rift basin was opened within a continent or a continental amalgamation. Subsequently, the basin evolved through accretionary process with subduction, formation of island arc and accretionary prism between India and East Antarctic cratons. Subduction took place toward the Indian side and sediments were metamorphosed and deformed with development of fold-thrust belt at the western margin against the Bastar Craton (Biswal and Sahoo, 1998). The mode then switched to the retreating one with subduction rollback and development of a back arc basin. Based on meager amount of geochronological data, we suggest that the basin was opened up due to rifting with the emplacement of alkaline magma at ca. 1.48 Ga (Upadhyay, 2008) and mafic magma at ca. 1.45 Ga (Shaw et al., 1997). Sediments deposited within the back arc basin were metamorphosed to UHT conditions (Sengupta et al. 1990, 1991) producing an anomalously hot orogen (Gupta, 2012). This was immediately followed by emplacement of voluminous charnockite–enderbite magma (0.98–0.96 Ga) both in Domain 2 (Paul et al., 1990; Aftalion et al., 1988; Bose et al., 2011) and in east Antarctica (Mawson Charnockite, Young et al., 1997). This post-kinematic igneous activity was related to deep crustal thermal perturbation following collision. The back arc as well as the open ocean basin gradually contracted due to closeness between the Indian and East Antarctic cratons. This finally caused closure of the basin through a series of accretion collision process.

However, the history of the Eastern Ghats Province continued further. The rocks of Domain 3 underwent multiple stages of tectonothermal reworking during Neoproterozoic time (0.80–0.50 Ga) (Simmat and Raith, 2008). Identification of late Neoproterozoic–Cambrian events in Domain 3 either suggests localized reworking of cratonized part of erstwhile Domain 2; or that Domain 3 represents an exotic unit, finally being amalgamated to India by ca. 0.5 Ga.

Metamorphic Evolution of Eastern Ghats Province

An early UHT (~1000°C) metamorphic event (M_1), north of the Godavari Rift at crustal depths of 30-35km (8- 10 kb) is reported from high-Mg-Al granulites in several areas. The earlier workers (Sengupta et al., 1990, 1991; Karmakar & Fukuoka 1998; Dasgupta and Sengupta 2003 and the references therein) argued for an anticlockwise trajectory for the prograde M_1 event under a fluid absent condition. From the considerations of petrogenetic grid they inferred that in the high-Mg-Al granulites, in the prograde path prior to the peak temperature, dehydration melting of biotite produced spinel + cordierite and cordierite + garnet assemblages in restites coexisting with the melt; sapphirine + ilmenite was produced by continuous reaction from spinel + quartz +r utile (Dasgupta et al. 1995; Sengupta et al. 1990). Peak M_1 P-T of 8-10 kb and ~1000°C led to, (a) breakdown of early cordierite in high-Mg-Al granulites and stabilization of sapphirine+quartz and spinel+quartz in appropriate bulk compositions and under suitable fO2 conditions (Sengupta et al. 1991; Dasgupta and Sengupta, 1995), (b) stabilization of wollastonite + scapolite + garnet (grandite) + calcite and wollastonite + anorthite + garnet (grandite) in calc-silicate granulites (Dasgupta and Sengupta, 1995, 2003), and (c) stabilization of spinel + anorthite + diopside + orthopyroxene + forsterite in mafic granulites (Dasgupta et al. 1991; Dasgupta et al.. 1993). Shaw and Arima (1996a, 1996b) deduced peak P-T conditions of 12 kb and 1100°C for the rocks at Rayagada, followed by decompression to 9 kb. , the retrograde path being characterized by isobaric cooling to 750°-850°C (Dasgupta and Sengupta, 2003 and references therein). The cooling produced orthopyroxene + sillimanite + garnet bearing assemblages in high-Mg-Al rocks by reactions involving spinel, saphirine, cordierite. It is inferred that post-peak isobaric cooling also produced K feldspar + cordierite + orthopyroxene symplectites in high-Mg-Al granulites through breakdown of osumilite (Dasgupta and Sengupta, 1995). The cooling produced coronal grossular-rich garnet and anorthite+calcite symplectite at the expense of scapolite + wollastonite + calcite assemblage in calc-silicate gneisses and coronal garnet over pyroxene in mafic granulites and enderbites (Dasgupta and Sengupta, 2003, and references therein; Mukhopadhyay and Bhattacharya, 1997).

According to several workers (Dasgupta and Sengupta, 2003; Das et al 2011)the isobarically cooled M_1 granulites were reworked by a second granulite grade metamorphism (M2) and partial melting, whose peak condition is estimated to be 8-8.5 kb and 800°-850°C, as constrained by the thermobarometric data. The gap between the M_1 and M_2 metamorphisms is marked by the intrusion of enderbite-charnockite into the supracrustal rocks. Leptynite and megacrystic garnetiferous gneiss are linked with the M_2 partial melting. The prograde path of M_2 could not be worked out. The retrograde path of M_2 is characterized by near isothermal decompression to ~5 kb as constrained by thermobarometric data. The formation of second generation of cordierite in pelitic gneisses at the expense of orthopyroxene + sillimanite + garnet + quartz, and of decomposition of garnet to anorthite + orthopyroxene/ ilmenite/ biotite is generally attributed to this decompression (Dasgupta et al. 1992, 1994, 1995; Gupta et al. 2000; Kamineni and Rao, 1988a; Mohan et al. 1997; Mukhopadhyay and Bhattacharya, 1997; Sengupta et al. 1990).

In many areas of the Eastern Ghats sporadic amphibolites facies metamorphism (M_3) accompanying hydration and carbonation has overprinted the earlier assemblages with P-T condition estimated at 4-5 kb, ~600° C. This is often localized along shear zones. In the Salur area Mukhopadhyay and Bhattacharya (1997) documented decomposition of garnet during such a low pressure cooling path following the isothermal decompression. This cooling trajectory is constrained by the following reactions,

Almandine + K-feldspar + H_2O = Muscovite + Annite + Quartz

Anorthite + K-feldspar + H_2O + CO_2 $\rightarrow$ Muscovite + Calcite + Quartz

STUDY AREA

Araku valley is situated in the NW of Vishakhapatnam city in Andhra Pradesh and is close to Orissa state border. The valley is on the Waltair Kirondal branch line, 119 km away from Waltair and 85 kms from Koraput. It comprises an area of 115 km. The valley is approximately in between 17°24’ N to 18°33’N latitudes and 78°24’E to 82°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.

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

OBJECTIVE OF THE PRESENT STUDY

1) Detail petrography and mineral chemistry of studied marble rocks.

2) Study of mineralogical evolution and reaction modelling.

3) Estimation of physical condition of metamorphism.

4) Delineating metamorphic events from the integrated studies mentioned above.

CHAPTER 2

FIELD DISPOSITION

Field relation:

The studied rock is extremely coarse grained representing a thick banded unit consisting of white coloured band and a grey coloured band (Fig 2.1.1.A).

The white coloured band comprises big calcite crystals of pegmatitic appearance. This layer has isolated crystals of brown coloured mica and mob coloured spinel visible under naked eye (Fig 2.1.1.B). The grey band is comparatively rich in silicate minerals than associated pure white coloured calcitic layer. High abundance of brown coloured biotite is noticed in both the layers. The mica grains are often concentrated to form clusters of mica. Thin disseminated needles as well as coarse flakes of graphite are present within this white coloured pegmatoidal calcitic rock. The thick interbanded unit show large folding exposed at quarry wall.

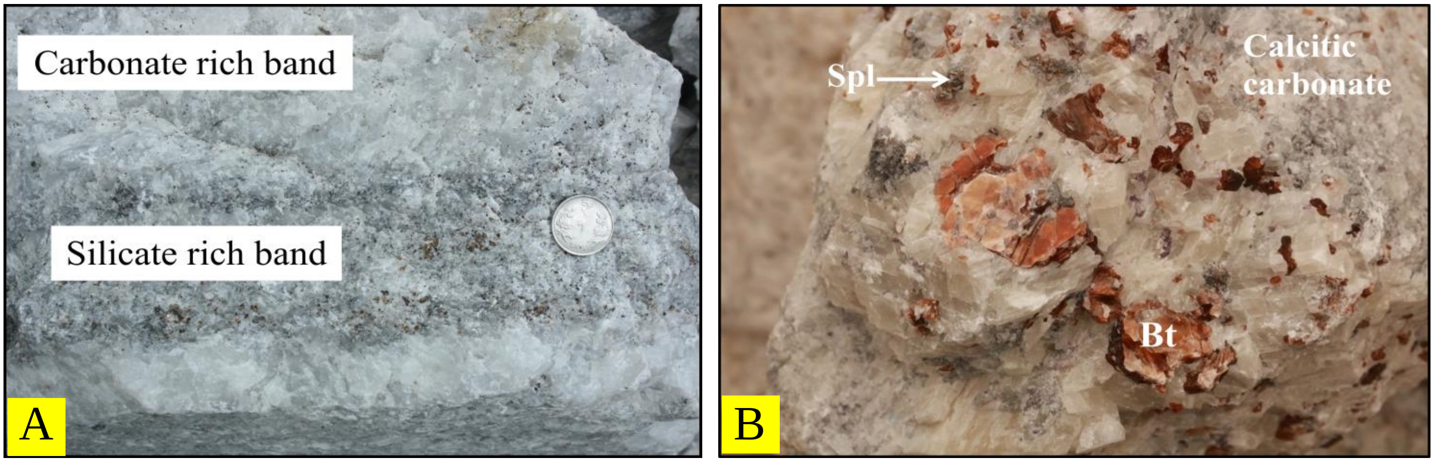

Fig 2.1.1: A: Band of silicate rich layer in coarse calcitic pegmatoidal carbonate rock

B: Occurrence of biotite cluster within calcitic carbonate

PETROGRAPHY

Mineral identification:

The studied marble rock is coarse to very coarse grained characterized by a mineral assemblage comprising of calcite, biotite, clinopyroxene, plagioclase, forsterite, spinel, amphibole and apatite. The minerals are identified under transmitted light microscope by the following optical properties:

1. ***Calcite (Cal):*** It is colourless, shows change of relief and surface roughness suggesting high to low refractive index under plane polarized light and under cross polarized light it shows mostly 4th order grey with distinct rhombohedral twinning.
2. ***Biotite (Bt):*** They are lath shaped, colourless and light yellow in colour, shows distinct pleochroism from colourless to shades of yellow and 1 set of cleavage with moderate refractive index. Very few grains show non-pleochroic nature. Under cross polarized light they show 2nd to 3rd order variegated interference colour with parallel extinction.
3. ***Clinopyroxene (Cpx):*** It appears colourless, non-pleochroic with high relief. 1 set of cleavage (out of two) in less fractured grains are observed under Plane polarized light. Interference colour is in the 2nd order showing inclined extinction.
4. ***Plagioclase (Pl):*** It is colourless with low relief. Under crossed polars it shows 1st order grey interference colour and distinct albite twinning.
5. ***Olivine (Ol):*** Colourless, high relief, non-pleochroic grains are observed under plane polarized light. Under croslled polars they show 2nd to 3rd order interference colour.
6. ***Spinel (Spl):*** It appears colourless, non pleochroic with high relief. Under crossed polars it is isotropic in nature.

7. ***Amphibole (Amp):*** It shows colourless, non-pleochroic grains with moderate relief and commonly found 1set of cleavage (out of 2). Under crossed polars it shows higher 2nd order interference colour.
8. ***Apatite (Ap):*** Colourless grains showing very high relief and non-pleochroic nature. They show 1st order interference colour.
9. ***Serpentine (Srp):*** Colourless, non pleochroic grains with low relief and 1st order variegated interference colour.

Textural observation:

The rock overall shows a banded appearance consisting of carbonate phase rich domain and silicate phase rich domain having grain size coarse to very coarse. The carbonate rich domain and silicate rich domains are represented here by association (a) and association (b) respectively.

Association (a):

The major constituents of this assemblage are calcite, biotiete, apatite, olivine, spinel, dolomite, clinopyroxene, amphibole, graphite and iron sulphide minerals.

Calcite occurs as i) mostly coarse grained rhombohedral crystals with well-developed grain boundaries, ii) small inclusions in other minerals. Calcite is present as inclusion within olivine (Fig 2.2.A), spinel (Fig 2.2.B) and apatite (Fig 2.2.C). The rock show overall granoblastic texture suggesting deformation and metamorphism. Exsolution textures of dolomite are observed within some coarse grained host calcite (Fig 2.2.D). The exsolution forms as lamellae, blebs of various shapes and worm like texture. The size of the exsolved lamellae varies length varying from

0.04mm to 0.6mm but size upto a maximum of 2 mm. The growth of exsolution varies in different grains. They are not visible or developed in all calcite grains present.

Biotite occurs as broad flakes of varying sizes ranging between 0.3 mm to 1.9 mm in length, set in calcite matrix as well as inclusions within different phases. Prismatic biotite flakes have straight boundaries. Sharp grain contact between biotite-spinel ((Fig 2.2.H) and biotite-calcite ((Fig 2.2.G) is prominent. Biotite is present as inclusion within calcite (Fig 2.2.F) and spinel (Fig 2.2.B).

Apatites are mostly sub-rounded to rounded in shape embedded within calcite matrix as interstitial phase. They stably coexist with calcite and shows granoblastic textural relation. Occasionally apatite grains exhibit distinct triple junctions with calcite (Fig 2.2.E). Apatites are also present within calcite grains and vice versa. Sharp boundary between biotite and apatite is common. Locally apatite is partially (Fig 2.2.C) or fully (Fig 2.2.I) recrystallized where partial recrystallization takes place along the margin of ovoid apatite grains.

Medium to coarse **olivine** grains are usually embedded within calcite matrix. Equilibrium boundary exists between olivine-calcite (Fig 2.2.A) and olivine-biotite (Fig 2.2.L). Megacrystic olivine grains are highly fractured and are partially or completely serpentinised (Fig 2.2.M). Spinel is partially or fully engulfed by olivine (Fig 2.2.A, K). Locally small rounded to subrounded grains of olivine are often enclosed within coarse calcite (Fig 2.2.J). Olivine is peripherally altered by clinoproxene in some places (Fig 2.2.K). Amphibole replaces olivine has disequilibrium boundary relation with amphibole (Fig 2.2.M).

Spinel is usually varies from fine to coarse grained. Coarse grained spinel are fractured and set primarily within calcite matrix (Fig 2.2.B). They are often intimately associated with olivine having smooth curvilinear boundaries in granoblastic texture (Fig 2.2.A). Locally spinel has calcite and biotite inclusions (Fig 2.2.B). Small spinel grains are engulfed within olivine (Fig 2.2.K). Amphibole overgrows spinel in some places (Fig 2.2.M). Patches of clinopyroxene are developed somewhere at the grain margins of spinel (Fig 2.2.M).

Amphibole occurs as elongated patches mainly replacing olivine and spinel (Fig 2.2.M).

Dolomite has no distinct grains and only occurs as anhedral exsolved blebs and lamellae within calcite host (Fig 2.2.D).

Association (b):

This assemblage is composed of calcite, biotite, apatite, clinopyroxene, plagioclase and graphite minerals.

Calcite is present as coarse granoblasts in matrix as well as relict xenomorphic patches with irregular boundaries associated with clinopyroxene and plagioclase. Inclusion of calcite is locally found within clinopyroxene (Fig 2.2.N) and plagioclase (Fig 2.2.O). Clinopyroxene (Fig 2.2.R) and plagioclase (Fig 2.2.S) are developing on the grain boundaries of calcite having usually corrugated boundaries with calcite.

Biotite occurs as broad flakes of varying sizes ranging between 1.9 mm to 0.3mm as well as inclusions within different phases. In most places, biotite grains appear to be invaded by clinopyroxene (Fig 2.2.R) and plagioclase (Fig 2.2.P) showing serrated boundaries. Locally cluster of biotite grains are deformed to form kink bandings (Fig 2.2.Q).

Biotite also occurs as patchy anhedral form replacing clinopyroxene, which also contains inclusion of calcite (Fig 2.2.T).

Subhedral **clinopyroxene** exhibits stable grain contact with plagioclase having curvilinear boundary (Fig 2.2.U). Clinopyroxene grains are showing resorbed boundaries with calcite and biotite. Often clinopyroxene patches protrude into calcite and biotite (Fig 2.2.R) from margins inward. Locally idiomorphic calcite and biotite are residing within clinopyroxene (Fig 2.2.N). In most places, clinopyroxene grains are fractured.

Plagioclase grains are mostly subhedral and shows straight equilibrium boundary with clinopyroxene (Fig 2.2.U). Plagioclase shows inclusion of calcite (Fig. 2.2.O) and disequilibrium boundary relation with both calcite (Fig 2.2.S) and biotite (Fig 2.2.P).

Mostly ovoid fine grained **apatites** are present. The apatite grains are embedded within grains of clinopyroxene. Sharp boundary relation exists between biotite and apatite.

Presence of **opaque minerals** is common within both the associations. Some opaques are tabular in nature mainly interstitial to other grains in few places. Some occur as elongated flakes present mainly along the boundaries of other minerals. Aggregates of elongated flakes at biotite-calcite boundary are occasionally showing a warp around biotite (Fig 2.2.V).

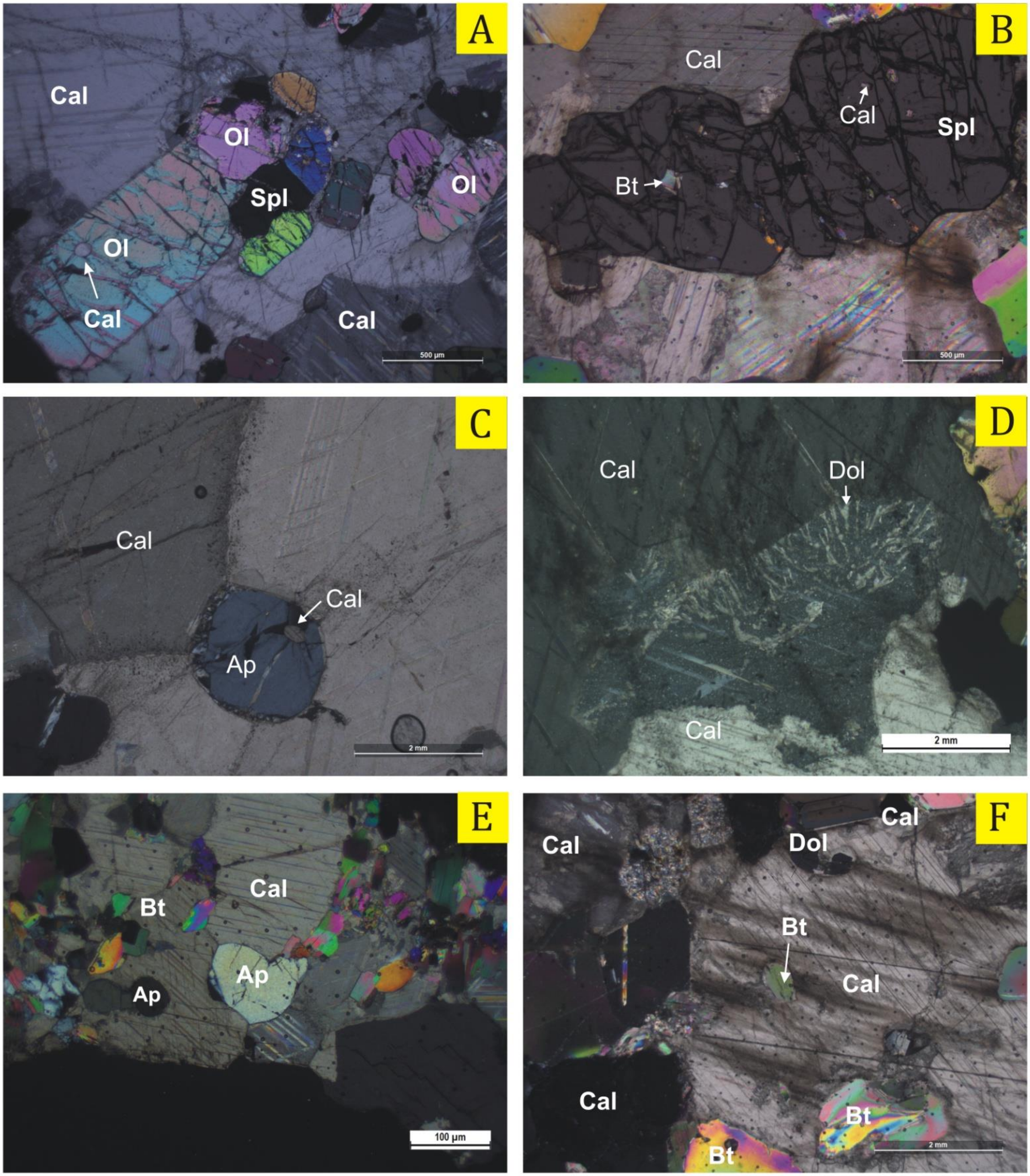

FIG 2.2:A: Calcite inclusion in olivine and spinel-olivine equilibrium boundary
B: Boundary between calcite and spinel and spinel showing biotite and calcite inclusions
C: Apatite recrystallised along its rim and calcite inclusion within apatite
D: Dolomite exsolution within calcite
E: Calcite-apatite triple junction
F: Biotite grain inclusion within calcite

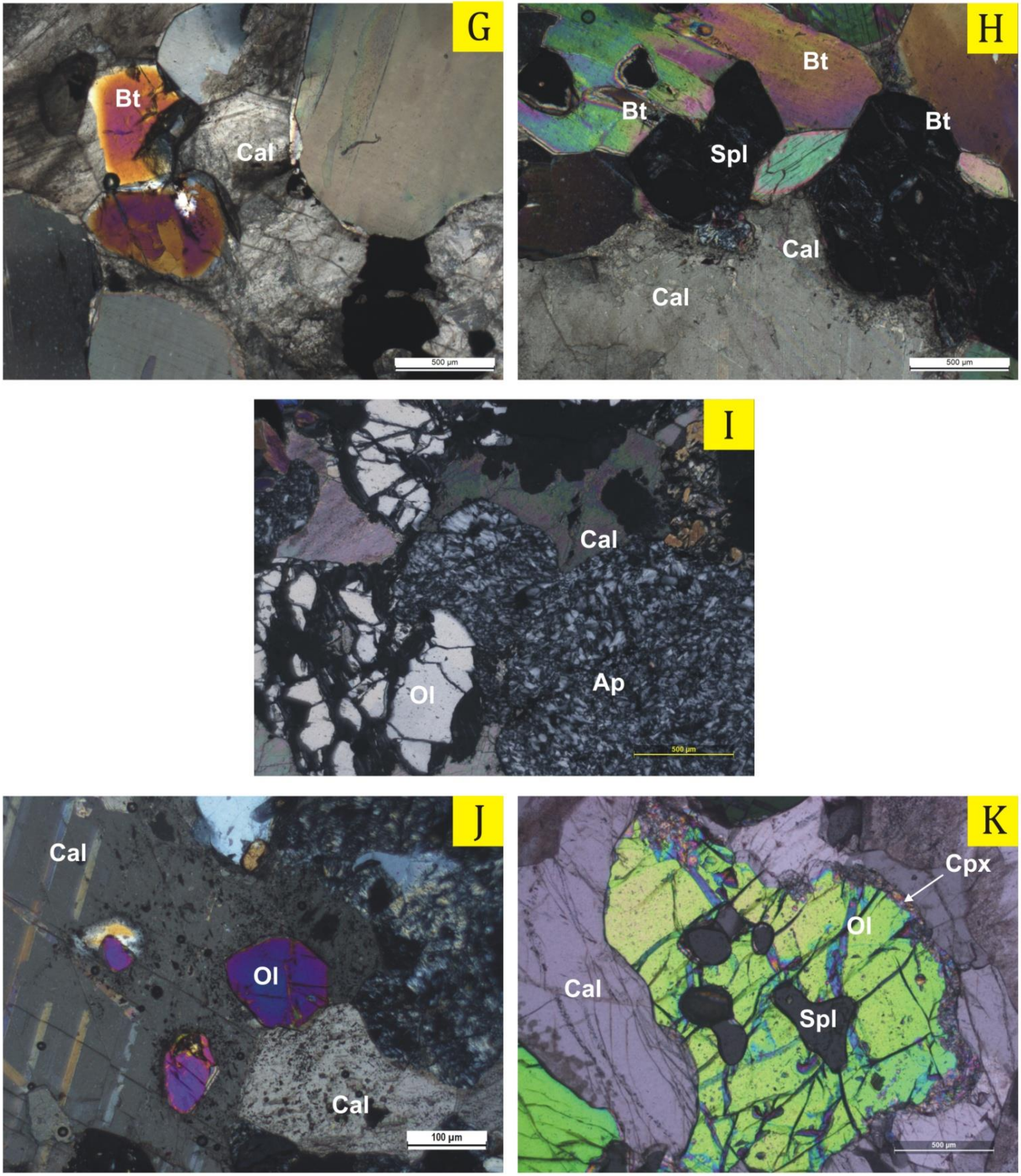

FIG 2.2:G: Calcite biotite straight boundary
H: Straight boundary between biotite and spinel
I: Recrystallised apatite
J: Olivine embedded within calcite matrix
K: Spinel inclusion within olivine and clinopyroxene rimming olivine

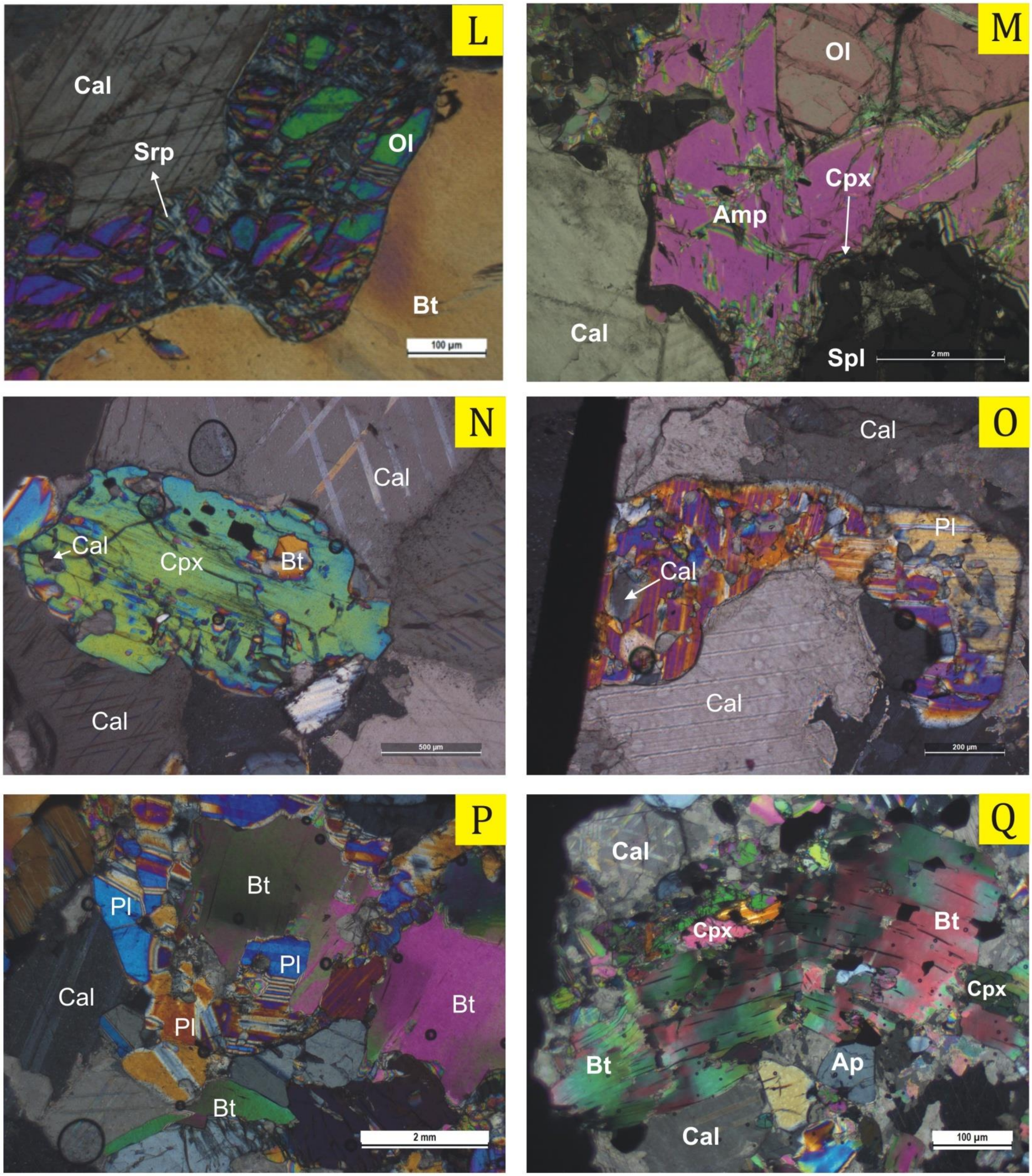

FIG 2.2:L:Fractured and serpentinized olivine
M: Olivine and spinel corrugated boundary with amphibole and clinopyroxene at contacts
N:Calcite and biotite inclusion in clinopyroxene
O: Calcite inclusion in plagioclase
P: Plagioclase replacing biotite
Q: Kinked biotite

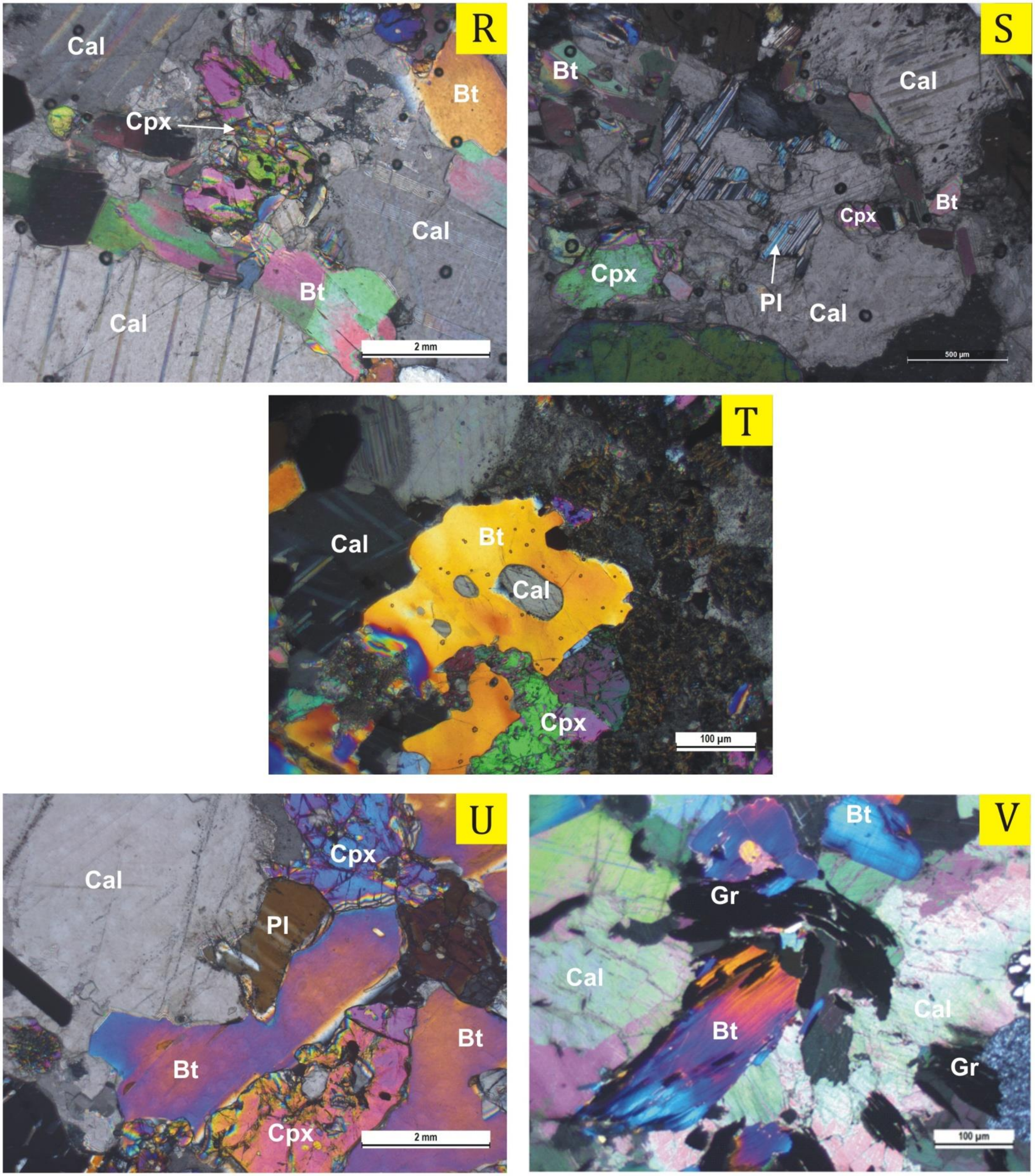

FIG 2.2 : R: Clinopyroxene protruding into calcite and biotite
S: Plagioclase replacing calcite
T: Anhedral biotite with calcite inclusion
U: Clinopyroxene-plagioclase equilibrium boundary
V: Aggregate of graphite flakes warping biotite

MINERAL CHEMISTRY

All the abbreviations of minerals used are according to Kretz (1983).

Selected phase chemical composition, done on electron probe micro analyser, has been provided by the supervisor only for the use of this unpublished M.Sc. dissertation. Structural formula has been recalculated from the provided oxide wt% of the mineral concerned.

Calcite

Calcite is almost pure $CaCO_3$. But it has some variable amount of Mg in its structure showing X_{mg} value varying from 0.0018 to 0.0597 (MgO in 0.078 to 2.83 wt%). Its composition is not purely homogenous and the core of calcite is more Mg rich and Mg decreases towards rim.

Biotite

Biotite is almost purely phlogopite (X_{mg}=0.97-0.99) in composition. It has a high alumina content (Al_2O_3 13-15 wt%), more than usual. Some amount of Ti (~0.4 a.p.f.u.) is present but Cr content is negligible in its structure. Low content of Ba is present and there is an increase in Ba from core to rim.

Clinopyroxene

Clinopyroxene is homogeonous in nature and almost purely diopsidic in composition (Fig 2.3.1) with a high X_{mg} value which varies from 0.978 to 0.992. It shows a high content of CaO and MgO followed by a low FeO content. Al_2O_3 content is variable (2.17-5.65 wt%) in different grains. Na_2O and TiO_2 contents are very low.

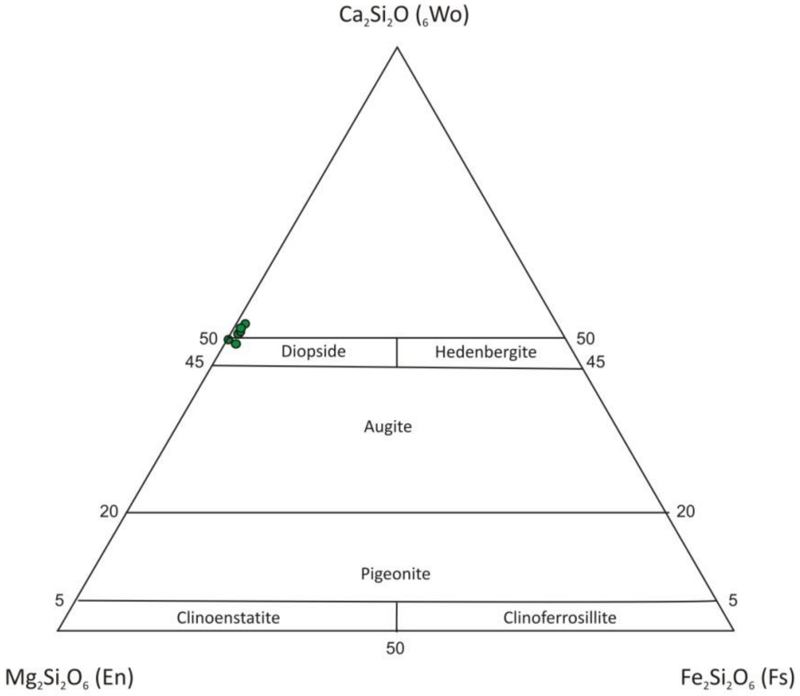

Fig 2.3.1 Pyroxene classification diagram

Spinel

It is Mg rich, homogenous in composition. The composition of spinel is more Mg-spinel (X_{mg}= 0.94-0.96) end member in spinel-hercynite solid solution. Some amount of Zn is present in its structure (ZnO-1.7-2.5 wt%). It is poor in Cr.

Olivine

Olivine is compositionally rich in Mg and falls towards forsterite (X_{Fo}=0.97-0.99) end member. They are homogenous in nature. They have negligible amount of CaO (less than 0.1 wt %). MnO is also present in very negligible quantity.

Plagioclase

Plagioclase is anorthite (Fig 2.3.2) rich (X_{an}=0.97-0.99) in albite-anorthite solid solution. It has a homogenous composition all throughout. K and B are absent in feldspar.

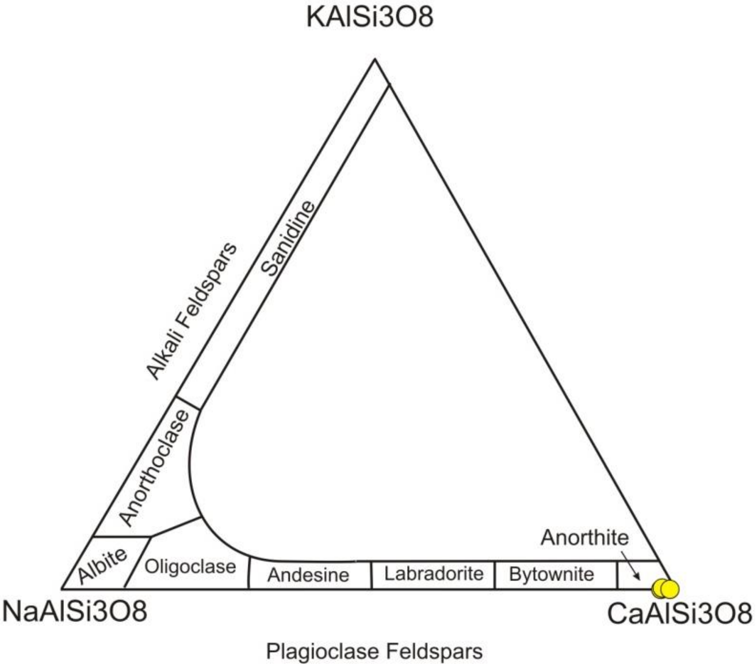

Fig 2.3.2 Feldspar classification diagram

Apatite

Apatite is homogenous in composition. It is F bearing where F content varies from 1.6-1.9 a.p.f.u wt% and negligible Cl (0.1-0.2 wt%) is present in its structure.

Dolomite

Dolomite shows high X_{mg} value of around 0.5. It has negligible amount of Fe in its structure (FeO~0.2 wt %).

Amphibole

Amphibole is pargasitic in composition (Fig2.3.3). It has a X_{mg} value of about 0.99. Some amount of Na (0.5-0.7 wt %) is present in its structure.

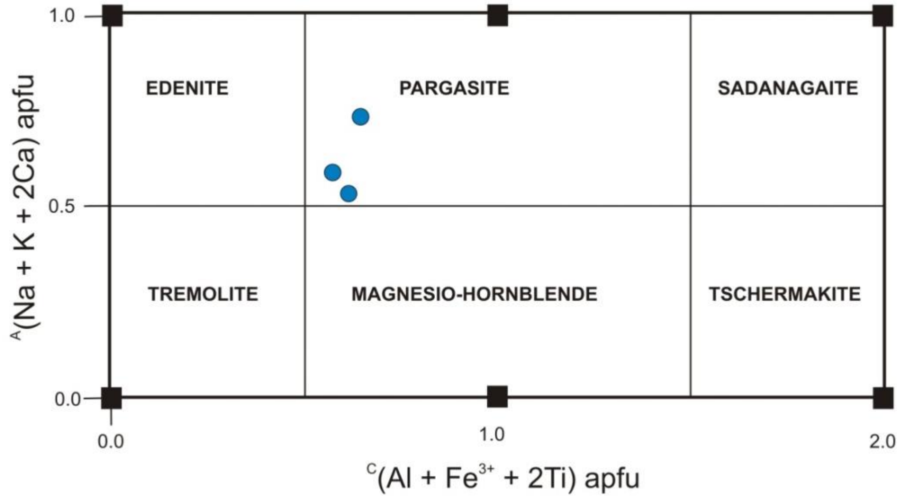

Fig 2.3.3 Amphibole classification diagram

The elongated flaky opaque minerals are identified as graphite and the tabular interstitial opaque minerals are mostly iron sulphides.

CHAPTER 1

MINERAL EVOLUTION

The association (a) consists of a assemblage of calcite + dolomite + phlogopite (Phl) + apatite + forsterite (Fo) + spinel + pargasite (Prg) + graphite (Gr) + iron sulfide and association (b) consists of assemblage of calcite + phlogopite + apatite + diopside (Di)+ anorthite (An) + graphite.

Association (a)

In association (a), forsterite shares smooth curvilinear boundary with calcite as granoblastic texture (Fig 2.2.A) in most of the places. Inclusion of phlogopite in calcite (Fig 2.2.F) and inclusions of calcite in forsterite (Fig 2.2.A) and both calcite and phlogopite inclusions in spinel (Fig 2.2.A, Fig 2.2.B) are noted in the textural description. The preponderance of calcite over forsterite and forsterite inclusions within calcite (Fig 2.2.J) are indicative of differential growth rate. Inclusions of spinel within forsterite (Fig 2.2.K) and their low abundance than the former are suggestive of higher growth rate of forsterite than spinel. The coexistence of forsterite + calcite + spinel indicates high temperature metamorphic event (Bol et al., 1989). Above textural features with compositional zoning of Mg in calcite suggest the following reaction (1);

$\text{Mg-Cal} + \text{Phl} \longrightarrow \text{Fo} + \text{Spl} + \text{Cal} + H_2O \pm CO_2$ ....(1)

Thin and some thicker rims of diopside around forsterite (Fig 2.2.K) indicate secondary formation of diopside after forsterite. As forsterite is forsteritic in composition this may be formed retrogressively following model reactions;

$2\text{Fo} + 4\text{Cal} + 2CO_2 = \text{Di} + 3\text{Do}$ ....(2)

Or,

$Fo + 2Cal + 3SiO_2 = 2Di + 2CO_2$ (Sauter, 1983). ....(3)

However, there is no signature of dolomite present along with diopside. Hence, diopside probably formed by the influx of a silica rich fluid following the reaction

$Fo + 2Cal + 3SiO_2 = 2Di + 2CO_2$ ....(4)

Amphibole is pargasitic in composition, which indicates presence of abundant aluminium in the rock. Amphibole shows a reactive boundary between spinel and forsterite (Fig 2.2.M), which gives the evidence for its possible formation mechanism from these two minerals. It is formed as a secondary mineral in retrogression.

$Cal + Fo + Sp + H_2O + Na \rightarrow Prg + CO_2$ ....(5)

Serpentine is formed along the fractures of deformed forsterite grains (Fig 2.2.L). It forms due to fluid-rock interaction during late stage hydration event. The fluid being supplied through the fractures reacts and forms hydrous serpentine mineral along the fractured zone.

$Fo + H_2O \rightarrow Srp$ ....(6)

Elongated blebs of dolomite grains within calcite megacryst (Fig 2.2.D) may be thought of as the product of exsolution. During retrogression, Mg-calcite cools and becomes supersaturated in Mg and finally dolomite phase starts exsolving. A lattice continuity across the interface between the exsolving phase and the host controlled by the elastic strain energy, results in the initial exsolution stage. The exsolution process is initiated with the formation of rod like dolomites, which grow and coalesce subsequently. The nucleation is irregularly distributed as exsolved lamellae of different sizes are observed in different parts of the calcite crystal. As the exsolution proceeds, the coherent lamellae thicken; elastic strain energy increases and widens to form blebs. The exsolved dolomite phase grows through the entire calcite crystal, if Mg content is higher.

Recrystallised apatite (Fig 2.2.I) in the rock is an indicator of deformation event. Crystalline aggregate of apatite lowers its free energy, which results in retrogressive misorientation of subgrains, accompanied by minor boundary migration. The granoblastic texture (Fig 2.2.E) present between calcite and apatite is suggestive of static recrystallization event during deformation.

Association (b)

In Association (b) diopside and anorthite both shows corrugated boundary relation with calcite (Fig 2.2.R, Fig 2.2.S) and phlogopite (Fig 2.2.P, Fig 2.2.R). Therefore, they are formed from the early calcite and phlogopite minerals. It requires addition of SiO_2 and Mg and removal of K as modelled by C-space program by Torres-Roldàn et al. (2000), The principles of C-space are described below.

Computer programme called C-space by Torres-Roldàn et al. (2000) solves an m × n matrix with the SVD technique and outputs all the possible balanced chemical reactions involving a given set of mineral compositions or chemical species. Out of the possible balanced chemical reactions, those explain the textural relations, are used for mass and energy balance calculations for a given metamorphic assemblage (Sengupta et al, 2009). The C-Space programme, which is based on the algorithm published by Fisher (1989, 1993) is, therefore, an elegant tool to model reaction textures that may help decipher the physico-chemical conditions, which a given rock might have evolved through (Lang et al. 2004).

Singular value decomposition or SVD technique used in C-space is a simple but robust technique that is widely used for modeling metamorphic textures (Lang and Rice 1985; Lang et al. 2004; Chowdhury et al, 2013 and the references cited therein). This technique checks linear dependencies and suggests possible reactions from a compositional matrix M of m minerals in terms of n components (Lang et al. 2004). SVD is a powerful method as it not only minimizes numerical errors but also provides solutions in cases where other methods fail to give satisfactory results (Press et. al. 1989).C-space runs based on the following theory:

A set of independently linear relations can be expressed as

$a_{11}X_1 + a_{12}X_2 + a_{13}X_3 + \ldots\ldots + a_{1n}X_n = Y_1$

$a_{21}X_1 + a_{22}X_2 + a_{23}X_3 + \ldots\ldots + a_{2n}X_n = Y_2$

$a_{31}X_1 + a_{32}X_2 + a_{33}X_3 + \ldots\ldots + a_{3n}X_n = Y_3$

$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$

$a_{m1}X_1 + a_{m2}X_2 + a_{m3}X_3 + \ldots\ldots + a_{mn}X_n = Y_m$

where m and n represent the total number of rows and columns of a given matrix.

This equations can be expressed in the form

$A.X = Y$ …(i)

where, A,X and Y are as follows:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13}\ldots\ldots\ldots\ldots a_{1n} \\ a_{21} & a_{22} & a_{23}\ldots\ldots\ldots\ldots a_{2n} \\ a_{31} & a_{12} & a_{33}\ldots\ldots\ldots\ldots a_{3n} \\ a_{21} & a_{22} & a_{23}\ldots\ldots\ldots\ldots a_{2n} \\ a_{31} & a_{12} & a_{33}\ldots\ldots\ldots\ldots a_{3n} \end{pmatrix} = A \quad \begin{pmatrix} X_1 \\ X_2 \\ X_3 \\ \ldots \\ X_m \end{pmatrix} = X \quad \begin{pmatrix} Y_1 \\ Y_2 \\ Y_3 \\ \ldots \\ Y_m \end{pmatrix} = Y$$

According to the SVD, an m x n matrix A (m=number of rows, n=number of columns), where m $\geq$ n , maybe expressed as

A = U.W.V ….(ii)

Combining the relations (1) and (2), we have,

U.W.V.X = Y ….(iii)

The relation (3) can be recast into the form,

W.z = d ….(iv)

where, z = VT.X and d = UT.Y

The relation (iv) can be solved to obtain the values of the unknowns from X_1 to Xn.

Now compositions of the m number of minerals or chemical species are linked by a chemical reaction and can be expressed in terms of n number of system components to generate an m×n matrix as in A of equation (i).

Using the mineral chemical composition of Mg-bearing calcite, phlogopite, diopside, anorthite the following diopside and anorthite forming mineral reaction has been modelled suing C-space;

14.2140 Calcite + 4.1065 Phlogopite + 13.7295 SiO2 = 12.9572 Diopside + 1.0000 Anorthite + 4.1095 K + 14.6357 CO2 + 4.1587 H_2O ....(7)

The kinked phlogopite flakes (Fig 2.2.R) are also indicative of deformation suffered by the rock. Occasionally the phlogopite flakes are closely spaced forming layers, which indicates an event of compression.

Apart from coarse prismatic one phlogopite also occurs as anhedral patchy habit replacing diopside containing calcite inclusion (Fig 2.2.T). It is suggested that the phlogopite could develop through the following mineral reaction during k-bearing silica rich fluid- rock interaction:

Mg-bearing Cal + k-bearing silica rich H_2O ± Di ⟶ Bt + Cal............(8)

GEOTHERMOMETRY

The technique of modelling and replicating some of the equilibria to evaluate the temperature at which a rock formed is known as Geothermometry. It is a work of experimental petrology, which involves calculation of equilibrium temperatures from the measured distribution of elements between coexisting phases. Geothermometers are those reactions that show considerable temperature sensitivity (large ΔH, ΔS) and small pressure sensitivity (small ΔV) and generally depicts those reactions that show considerable temperature sensitivity (large ΔH, ΔS) and small pressure sensitivity (small ΔV) and generally depict the solid-solid reactions that do not have any effect of partial pressure of fluid species.

Types of geothermometers:

1. Ion exchange
2. Solvus

- Ion Exchange :

  It involves the exchange of cations with similar sizes and charges between two minerals. These reactions are typically very temperature-sensitive, with no major change in volume involved in the exchange. They are further divided into intra-crystalline exchange which involve interchange of two similar atoms and inter-crystalline exchange which is an exchange between different sites in one mineral by intense diffusion process. Common exchange thermometers are Garnet–Orthopyroxene, Garnet-Clinoproxene etc.

- Solvus :

  Solvus thermometers are based on the miscibility gap or solvus in a temperature composition (T-X) space between structurally related phases. These phases form a solid solution at high-T but 'unmix' into separate phases during cooling. The composition of coexisting minerals that have a solvus relationship are indicators of temperature. They represent part of the cooling path of a rock. Common solvus thermometers are Two-pyroxene thermometers, Two-feldspar thermometers, Calcite-Dolomite thermometers etc.

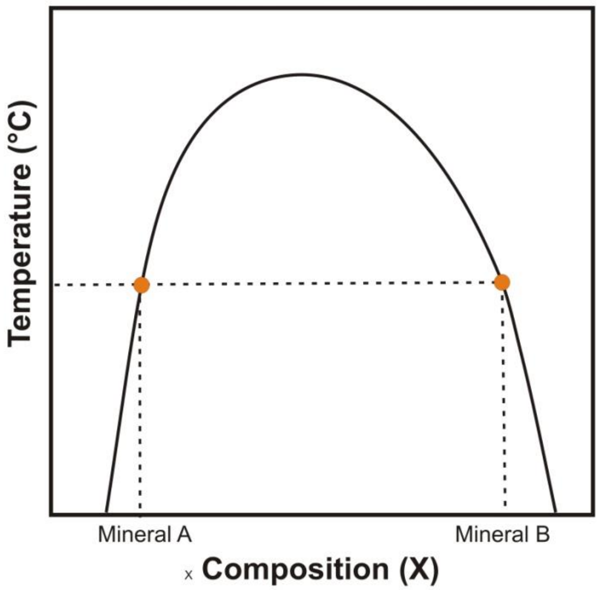

Fig 3.2.1: A solvus curve in a schematic T-X phase diagram

Calcite-dolomite solvus thermometry:

Calcite-dolomite solvus thermometry is a commonly used geothermometer for marbles. Experimentally and thermodynamically this thermometer has been well calibrated (Goldsmith & Newton, 1969; Powell et al., 1984; Anovitz & Essene, 1987). Mg content in calcite is controlled by crystal growth rate, diffusion and exsolution. The reintegrated composition of calcite and dolomite is usually applied to determine the peak metamorphic temperature. The morphology and of the unmixed phase is important for re-integration of Mg-content in calcite and further temperature studies.

In the studied rock, petrography and analysis of BSE image are used for morphological characterization of unmixed dolomite. In different unmixed zones within a single grain, the compositions of dolomite lamellae and host calcite are reintegrated to deduce the peak temperature.

Calcite−dolomite solvus geothermometry was applied using the formulation (23) of

Anovitz & Essene (1987) as given in the following:

$$\mathbf{T_{(K)} = A\,(X_{Mg}) + B\,/(X_{Mg})^2 + C\,(X_{Mg})^2 + D\,(X_{Mg})^{0.5} + E} \text{ ....(1)}$$

where A, B, C, D and E are coefficients with values -2360.0, -0.01345, 2620.0, 2608.0 and 334.0, respectively, and X_{Mg} is the Mg content [Mg ⁄(Ca+Mg) a.p.f.u.] of calcite.

Although this formulation does not account for Fe in the system, it is still suitable for this study because Fe was barely detected in the carbonates.

Another equation derived by Puhan (1979) through his experimental data is used to calculate the temperature and The Mg-content of calcites, expressed as mole percent MgC03 was used to evaluate the data.

$\log X_{MgC03} = -1414/ T(°K) + 0.4869$ ....(2)

This equation is applied for both the unmixed calcite from which dolomite is exsolved and the reintegrated calcite-dolomite, which represents the initial composition of the calcite.

Results:

3 grains of calcite were studied. To which, applying the formula of Anovitz & Essene (1987) yielded a temperature range of 482-571°C (Table 3.2.1), matches well with the temperature range 476-562°C (Table 3.2.1) derived from equation of Puhan (1979). Then, 3 domains of homogenously distributed exsolved dolomite in calcite matrix were analysed and reintegrated by estimating a composition prior to unmixing, from the present compositional data and estimating the area of calcite and dolomite using a digital BSE image. This yielded a temperature ranging between 805-869°C (Anovitz & Essene, 1987) (Table 3.2.1) and 775-822°C (Puhan, 1979) (Table 3.2.1).

Table 3.2.1: Calculated temperatures from calcite-dolomite solvus geothermometric equations

	Unmixed calcite matrix	Reintegrated calcite-dolomite
Calculated temperature (in °K) according to Anovitz & Essene (1987)	790.187	1142.331
	755.866	1087.634
	844.951	1078.338
Calculated temperature (in °K) according to Puhaan (1979)	781.066	1095.909
	749.187	1055.147
	835.826	1048.135

So for both the equations, the calcite matrix yields a lower temperature than the reintegrated calcite composition, which indicates that the peak temperature was at least this temperature or even higher. This is thoroughly justified as the exsolved calcite host diffuses Mg phase during retrogression forming blebs and lamellae of dolomite. Thus decreasing Mg content in its structure and yielding a lower temperature than the actual temperature of formation. The lowest temperature estimates calculated in unmixed calcite matrix in our study possibly indicates the closure temperature of Mg diffusion and unmixing during cooling.

DISCUSSION

DISCUSSION

The studied rock is extremely coarse grained thick banded marble unit megascopically consisting of two distinct bands- a white coloured band predominating over alternating grey coloured band. The white coloured band in hand specimen shows very coarse (sometime pegmatitic in appearance) calcite crystals with mob coloured spinel and blue coloured apatite. The grey band is rich in silicate minerals like pyroxene and anorthite. High abundance of brown coloured biotite is noticed in both the layers. Both the units are graphite bearing. However, it is abundant in white coloured coarse calcitic marble and occasional in grey coloured marble layer. Two marble bands within the rock unit are represented by two distinct mineral assemblages as studied in petrography. Silicate mineral compositions are close to magnesian end member composition and calcite grains is magnesium bearing.

The carbonate rich layer (called association (a)) consisting of predominantly very coarse calcite with accessory biotite (phlogopite), olivine (forsterite), spinel, apatite, dolomite, clinopyroxene (diopside) and amphibole with overall a granobloastic texture. Integrating textural relation and composition of minerals the peak assemblage of association (a) can be determined as calcite + olivine+ spinel + (apatite + graphite + sulphide) characterized by equilibrium relationship of the constituent minerals. The coexistence of olivine + calcite + spinel indicates high temperature metamorphic event (Bol et al., 1989). Incusion textures in association (a) suggest that the peak calcite-olivine-spinel assemblage could develop from breakdown of biotite and Mg-bearing calcite. Zoning in calcite indicates deplesion of Mg from core to rim, which explains consumption of Mg to develop the peak assemblage through the mineral reaction. Clinopyroxene, amphibole and serpentine formed as retrograde phases and hence depict retrograde metamorphic event. Coarse grained granoblastic texture, recrystallisation, and kinking in biotite grains are clear indicative of deformation-metamorphism event. Exsolution of dolomite in calcite is a notable feature in this marble. It suggests peak metamorphic temperature reaches at least above the solvus temperature and the rock cooled below the solvus from peak temperature.

The silicate rich band contains relatively less carbonate phases compared to the white coloured band. The assemblage is characterized by calcite, biotite (phlogopite), clinopyroxene (diopside), plagioclase (anorthite) and apatite. Presence of granoblastic texture, recrystallization, inclusion reaction textures and kinking in biotite are indicative of deformation – metamorphism in the marble. Textural relationship suggests that peak metamorphic assemblage was calcite + clinopyroxene + anorthite. Inclusion texture suggests that the peak assemblage was stabilized through the consumption of calcite and biotite. Patchy biotite formed as retrograde phase during cooling of the rock.

Geothermometric study of the rock assemblage is done by the calcite-dolomite solvus geothermometer, which yields temperature range of 482-571°C of the host Mg-bearing calcite after exsoulution using formula of Anovitz & Essene (1987), well consistent with the obtained temperature range 476-562°C (Puhan, 1979). The reintegrated composition of host calcite and exsolved dolomite lamellae yields temperature ranging between 805-869°C (Anovitz & Essene, 1987) and 775-822°C (Puhan, 1979). The calcite matrix yields a lower temperature than the reintegrated calcite composition. Therefore, it may be concluded that peak metamorphic temperature was at least above ~850^{O}C. Exsolution of dolomite in calcite suggest a retrograde cooling event. Decreasing Mg content in the structure of Mg-bearing calcite and yielding a lower temperature from the host grains indicate that the cooling continued till ~500^{O}C temperature.

Therefore, studied coarse-grained calcitic marble records a high temperature granulite grade metamorphic event followed by a retrograde cooling event suggesting ~300^{O}C temperature drop.

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