PETROGRAPHY AND GEOCHEMISTRY OF LIMESTONES FROM PARTS OF PHEK DISTRICT, NAGALAND WITH REFERENCE TO GENESIS AND ECONOMIC VIABILITY

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DECLARATION

I, Mr**. Sheyamong Pechongri,** do hereby declare that the subject matter of this thesis is the record of the investigations done by me under the supervision of Dr. B.V. Rao Professor and Head, Department of Geology, Nagaland University, Kohima Campus, Meriema. The work contained in this thesis is original and in part or in full, has not been submitted by me for any research degree to any other university/Institute.

This thesis is being submitted to the Nagaland University for the award of degree of Doctor of Philosophy degree in Geology

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Certificate

This is to certify that the thesis entitled "Hydro-geochemical studies of groundwater in parts of Dimapur district with special reference to groundwater quality" submitted by **Mr. Sheyamong Pechongri** bearing Registration No: 622/2014, 20th May 2014 for the degree of Doctorate of Philosophy in Geology, Nagaland University is based on the work carried out by him under my supervision and guidance.

I certify that the work contained in this thesis has not been previously submitted for any degree /diploma or any academic award to any University/Institute and that the sources from which ideas are borrowed have been duly referred to. The candidate has fulfilled all conditions laid down by the university.

BVRao

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CONTENTS

CHAPTER I

INTRODUCTION

1. INTRODUCTION

Nagaland is the sixteenth state of the Indian Union and geographically it lies towards the North- Eastern part of India bordering Myanmar in the East, Arunachal Pradesh in the North-West, Assam in the West and Manipur in the South. The state covers a total area of 16,527 sq. km. The Naga Hills are the westernmost, morpho-tectonic unit of the Myanmar orogeny that continues into the eastern syntaxial bend of the Himalayas in the north. The central lowlands of Myanmar lie on its east and the Mikir Hills Precambrian Massif and the Brahmaputra trough containing Miocene to Quaternary sediments lie in the west.

The ophiolites of Naga Ophiolite Belt (NOB) are rootless blocks of various dimensions, floating in a matrix, which belongs to the Upper Cretaceous-Lower Tertiary Disang Group. They consist of diverse igneous, sedimentary and metamorphic rocks of which ultramafics are the main component. They do not constitute a continues sheet but made up of units randomly juxtaposed along faults or they consist of lensoid slices interbedded with Disang Group rocks (Bhattacharjee, 1991).

The NOB is a part of the Naga–Arakan Yoma flysch trough of Upper Cretaceous to Middle Eocene age, occurs along the Indo- Myanmar border, extending over 90 km. in length and 2-15 km in width, and covers an area of about 1000 sq. km. In the central part of the area, the NOB is exposed as an arcuate linear belt between the Disang Group on the west and the Nimi Formation towards the east. Being sandwiched between the Disangs and the Nimi Formation, their transport into the Disang flysch and, in turn, been over-ridden by the Nimi Formation from the east is an evidence that the NOB have tectonic contacts on either side. The highly dismembered and slices of the Ophiolites of varying dimensions are arranged in NE-SW to NNE trending 'en *echelon'* patterns with sub-parallel tectonic inter-relations.

Tectonically, the NOB is a Tethyan oceanic crust and upper mantle generated at a spreading centre in a narrow, short-lived basin, which was formed due to rifting and spreading during the Late Cretaceous. The opening and closure of this basin was related to the fragmentation and dispersion of Gondwanaland. The oceanic crust, thus generated, was later tectonically uplifted along with the upper mantle along a passive continental margin of the Indian plate by the end of the Eocene. This is evidenced by an interesting geomorphic feature of the belt, where a natural stagnant water body called Shilloi lake, located at Lütsam (Lacham) occupies a topographically low area formed of volcanic while serpentinites occur at higher level all around the lake.

Topographically, the Ophiolite belt, resembling any young mountain terrain, constitutes the northern part of Indo-Myanmar Orogeny with rugged, inaccessible terrains, high hills, sharp crests, narrow valleys and deep gorges. The general altitude varies from 920 m (Lütsam/ Lacham Lake) to about 3800 m (Mt. Saramati) above mean sea level. The NOB is one of the least geologically documented terrains due to the inaccessible nature of the area.

The ophiolite suite of the rocks comprises mainly mafic-volcanics, mafic-ultramafic cumulates, plagiogranite, volcanogenic sediments and late felsic intrusives. Mafic and ultramafic rocks constitute a major component of the NOB. The ultramafic and mafic cumulates are represented mainly by peridotites, pyroxenites and gabbros.

Limestones are found in association with chert and volcanics in the Ophiolite Belt. They occur as small to large detached bands and lenses, often with sheared contacts with the host rocks. They trend N-S to NE-SW with sub-vertical dips on either side. They are fine to coarse-grained crystalline rocks with colours varying from pale to dark grey. The important deposits are exposed at Wazeho, Shatüza (Satuza), Laruri, Phokhungri, New Thewati, Zhipu (Zipu) and Mokie (Moki), and villages of Phek District, Nagaland.

1.1 LOCATION

The present study area falls under the Meluri sub-division of Phek District, Nagaland (NE India) and is a part of the Naga Ophiolite Belt (NOB) extending between the parallels 25°33′40″ N to 25°44′0″ N latitude and 94°41′40″ E to 94°52′0″ E longitude covering around 329 sq. km. The area of investigation forms a part of Survey of India Toposheet No. 83K/14 (Fig. No. 2).

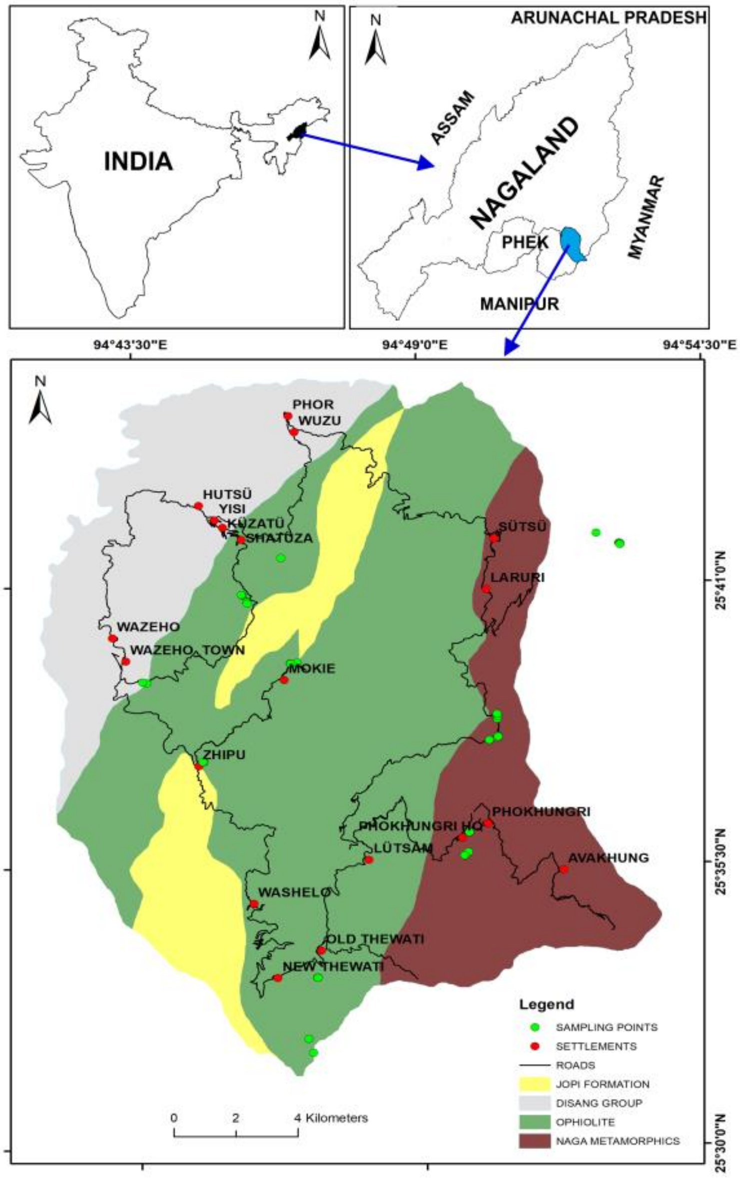

Fig. No. 01: Location Map

1.2 ACCESSIBILITY AND COMMUNICATION

The study area, however situated in the remote and a challenging terrain in the interior part of Nagaland along the Indo-Myanmar boundary, is accessible by an all weathered mineral road starting from Akhegwo to Phokhungri via Wazeho- Zhipu- Washelo. All the aforesaid study area except for Mokie have helipads constructed by the State Government to facilitate the exploratory activities of the Directorate of Geology and Mining. Wazeho being the centre of the area and is connected to Meluri, the main supply and communication centre for the region and lies at a distance of 240 km from Dimapur along NH-155 that passes through Kohima and Pfutsero.

Dimapur, the commercial hub of Nagaland is the only railway station and air-port in Nagaland connecting the state to other parts of the country. Wazeho also happened to be the base station of the study area (Shatüza, Zhipu and Mokie). New Thewati happened to be another base station to cover Laruri and Phokhungri.

1.3 PHYSIOGRAPHY

Physiographically, the study area depicts a panoramic and picturesque landscape of the surrounding hills and mountain ranges forming a part of the Arakan-Yoma- Patkai mountain ranges of the eastern part of Nagaland. The mountain ranges are consisting of series of Northeast trending sub-parallel ridges and valleys. The hills and mountain ranges, in general, gain altitude eastward one after another culminating at Nazüpfu (2357 m above msl) while the western boundary is controlled by the Jopi-Zephuhu range. The total area of the present study is about 329 sq. km. In general, the area mostly is a rugged terrain with high hills, deep gorges and narrow valleys.

Lütsam (or, Shilloi) Lake is the lowest elevation in the area about 900 m. This lake is one of the most beautiful lakes in Nagaland. The origin of the lake is still debated amongst the Geoscientists as to whether the lake is a remnant of a volcanic crater, a meteoritic impact or a tectonic origin lake. There are so many human extra perception stories about the origin and existence of the lake, which has made the lake famous in the North–East. However, the unique geological set-up and the scenic topography of the area is most interesting for the Earth scientists, added to which, the thick and variegated flora and fauna, pleasant climatic condition around the lake, are the source of attractions for the local and outside tourist.

1.4 DRAINAGE

The drainage systems are mostly structural controlled with dentritic to sub-trellis pattern. Tizü and Lüyakti river forms the main watershed catchment drainage system in the area, which flows in a northerly direction. Besides, there are Khayowti river, Chizüti and Yowthrüti creek. These creeks along with low order streams and rivulet joins Lüyakti river that flows northerly and ultimately join into the main Tizü River in the west which is a major river in the eastern Nagaland that flows into Myanmar.

1.5 CLIMATE AND RAINFALL

The area falls under Sub-tropical to temperate climatic condition with cold to moderate weather. Winter falls between the months of November to January, which are very cold with ground frost, and occasional snow falls. Summer falls between June to mid-September with short duration of spring from February to May and short autumn from end of September to October. The area receives heavy rainfall during the monsoon. November to April is the best period for any kind of work, expedition, hiking etc in this region.

1.6 FLORA AND FAUNA

The study area is rich in flora and fauna. During the British dominance over Nagaland in the early 1930s, this area was declared as reserved forest and protected area. Uninhabited areas are mostly covered with thick vegetation. The vegetation includes subtropical forests with local patches of cultivation along hill slopes. The sedimentaries and volcanics is generally observed with thick vegetative cover whereas the ultramafics are either thinly vegetated or barren. Of all the major floras, Pine is the most dominant while the others include oak, chestnut, palm, gooseberry, rhododendron, bamboo, fern, exotic varieties of orchids etc.

However, when the mineral road reached the area, the valued trees were cut down for timber business; otherwise the area was dense in vegetation with trees like Pines, Bonsum, Titachap, Kokhon etc. with varieties of Orchids. The area is also habited by wild animals like Deer, Tiger, Bear, Wild Boar, Snakes, Monkeys, Flying Squirrel and birds like the rare Blythes' Tragopan, Pheasants, Doves, Eagles, Hornbills etc.

1.7 HUMAN HABITATION

The Pochury Naga tribe with 32 villages inhabits the area. The population of the area is scanty and the village population ranges from 450–3000. Apart from Pochury people, the area is also inhabited by other Naga tribes including Chakhesang, Sangtam, Sumis, Aos, Lothas and Yimkhiung etc. The Cultural, intellectual and lingual of the different tribes are similar, though in some cases, the rituals and customs vary to a minor extend. Most of the people are conscious of their ethnological characteristics, and proud of their customs, rituals and tradition. Most of the villages are situated in the hilltop. People are simple, honest and hardworking by nature. Agriculture is their main occupation. Jhum cultivation is widely practiced along the hills slope and only few villages could adopt terraced cultivation along the valleys. Hunting and fishing are also a part of their occupation since time immemorial.

1.8 PREVIOUS LITERATURE

The earliest published reference to Nagaland Ophiolite Belt dates back to early 20th century. Due to poor accessibility, rugged topography and thick sub-tropical forests, systematic geological mapping in this terrain was not possible until the late sixties. However, the ultrmafics rocks of Manipur part of the Ophiolite belt were recorded by R.D. Oldham (1883). Sir Edwin Pascoe accompanied a punitive expedition to the Saramati peak, and completed a few traverse (Pasoe, 1912). The only earlier record of geological interest in respect of the eastern parts of Naga Hills is available from the reports of the geological traverses made by Oldham (1883) and Pascoe (1912). Mathur and Evans (1964) established the stratigraphy of Assam and Nagaland. With the formation of the state Directorate of Geology and Mining (DGM) during the latter part of 1968 more importance was given to unravel the geology and mineral resources in the eastern part of the state. This led to the defining of a stratigraphic sequence for the rocks of Nagaland (1978).

Systematic geological mapping of the NO Belt had been undertaken by the geologists of the Geological Survey of India (GSI) and DGM, Nagaland (Bhaumik and Majumder, 1974; Chattopadhyay and Roy, 1975; Agrawal, 1977; Srivastava et al, 1978; Agrawal and Kacker, 1980; and Roy and Kacker, 1980). The available geological details of the Ophiolite Belt were synthesized in several recent publications by Sen and Chattopadhyay (1978), Chattopadhyay et al, (1983) and Kacker et al, (1984). Based on palaeontological records the age of the ophiolites has been placed from Upper Cretaceous to Eocene (Chattopadhyay et al, 1983).

Petrography and geochemistry of the ophiolites, particularly the limestone was initiated by Agrawal and Ghose (1971, 1979 and 1982), and Chattopadhyay et al, (1983). Agrawal and Changmai (1978), Rao (1982), Rao and Kikon (1988) carried out detailed geological mapping and sampling of the Limestone deposits from Wazeho, Shatüza and Mokie to assess its general quality and quantity. Sibdas and Goswami (1986) Singh *et al* (1989), Subba Rao *et al* (2004 & 05) have worked on geology, mineral occurrence and metallogenetic aspects in Naga Hills Ophiolite Belt.
All these workers have distinguished the existence of litho-assemblages of dismembered bodies of the ophiolite. Rao BV et. al (2005), Rao (2006), Srikanth et. al (2004), Subba Rao et. al (2004) and Balaram et. al (2004 and 2006), B.V.Rao and Ranjit Nayak (2016), Ranjit Nayak and B.V.Rao (2017), BV Rao et al (2021) further contributed lot to the geology with reference to petrology and geochemistry of NOB.

The Indo-Burman geology is very complex owing to its involvement in subduction related crustal processes leading to polyphase magmatism, sedimentation, deformation and metamorphism at an ancient continental margin (Agrawal, 1976; Srivastava et al, 1978; Ghose and Singh, 1981; Ghose, 1980; Agrawal and Kacker, 1980; Roy and Kacker, 1983; Roy and Chattopadhyay, 1982; Chattopadhyay et al, 1983; Venkataramana et al, 1984; Agrawal and Ghose, 1986; Ghose et al, 1986). Based on the morpho-tectonic elements, the Naga Hills has been longitudinally divided, from west to east, into three distinct units, namely- the Schuppen Belt, the Inner fold and the Ophiolite Belt.

The hypothesis on plate tectonics added a new dimension to the metallogenetic expectation of the Ophiolite Belt as a possible locale of massive sulphides, chromites and nickeliferous laterites which provided fresh impetus for renewed efforts in systematic studies of the entire Ophiolite Belt for locating mineral deposits.

1.9 AIM AND SCOPE OF WORK

The Naga Ophiolite Belt is one of the best-developed terrain in contrast to other ophiolites in India. Ophiolites have evoked much interest in exploration geologists and have proved potential sites for several mineral deposits like cobalt-nickel bearing magnetite, chromite, base metals (Cu, Pb and Zn), limestone, etc. and constitute favourable locales for the deposition of precious metals like PGE and gold. Consequently, the ophiolites are being explored throughout the world for their mineral wealth. The ophiolites also offer important clues to the history of crustal evolution and geodynamic development on the northeast margin of the Indian subcontinent

Not much detailed work has been carried on petrography, geochemistry, genesis and economic viability of limestones etc., particularly, in the study area except for some minor investigations by the GSI and DGM.

In this context, the present investigation is an attempt to throw light on their genesis and economic viability of the limestones by extensive studies including field relationships, petrography and geochemistry. The following objectives were undertaken to achieve during the course of study:

- To carryout detailed field work of the study area including collection of rock samples of limestones and associated rocks,
- To carryout petrographic study of limestones and associated rocks.
- To analyse whole rock chemistry (major oxides, trace and REE) and to decipher the genesis and economic viability of limestone by using modern petrochemical plotting.

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CHAPTER II

GEOLOGICAL SETTING

2.1 REGIONAL GEOLOGY

Nagaland forms a part of the Indo-Myanmar Orogenic Belt which extends northward into the Eastern Syntaxial Bend of the Himalayas and southward through the Andaman and Nicobar Islands to the Mentawai group of islands southwest of Sumatra. The Indo-Myanmar orogenic belt covers a massive area within the states of Assam, Nagaland, Manipur, Mizoram and Tripura. The Dauki-Disang Tear Fault separates the orogenic belt from the Mikir Massif craton and the Naga Thrust separates the same from the Brahmaputra valley. The alluvium of Bangladesh covers the western portion of the belt while the eastern portion merges with Cenozoic sediments of the Central Lowlands of Myanmar (Mitchell & McKerrow, 1975), (Fig. No. 2).

The Naga orogenic belt can be broadly divided into four distinct tectono-stratigraphic units (Ghose and Singh 1981; Venkataramana *et al* 1986; Ghose and Agrawal, 1989). These are: (i) Belt of Schuppen: a sedimentary nappe of Eocene-Upper Miocene age separated by Disang thrust, along which the Naga Hills have relatively moved towards northwest (Evans 1964;Dasgupta 1977), (ii) Disang: a thick pile of clastic flyschoid sediments dominantly argillaceous of Upper Cretaceous-Eocene age derived from the Proterozoic hinterland of the Indian shield and Myanmar (Chattopadhyay *et al*. 1983), (iii) Ophiolite: a suite of magmatic, metamorphic and marine sediments of Maestrichtian–Palaeocene age based on macro- and micro-fossil evidences (Bender 1983;Acharyya *et al*. 1986) and (iv) Nimi/Naga Metamorphics: a low-grade pelitic-psammitic and carbonate sequence of Mesozoic/Proterozoic age, occupying the eastern fringes of India and Myanmar. The Nimi Formation forms a sedimentary cover sequence of accretionary prism (Agrawal 1985; Agrawal and Ghose 1986), overlying the Naga Metamorphics possibly representing the basement

(Acharyya et al. 1986). Presence of plant fossils and carbonaceous matter suggest a humid climate and paralic depositional environment for cover sediments. It is least deformed and attributed to be Eocene (Acharyya et al. 1986) or Oligocene (Agrawal and Ghose 1986).

The Naga Orogenic Belt is bounded on the west by the Precambrian Mikir Massif of Assam, with peripheral Tertiary shelf sediments on the northwest by Brahmaputra trough lineaments. The Naga Ophiolite Belt (NOB), confined along the eastern margin of this orogen, is bounded on the east by Cenozoic sediments of the Central Lowlands of Myanmar and on the west by a tectonic pile of Tertiary over-thrusts known as "*Belt of Schuppen*" (Mathur & Evans, 1964) and Disang flysch sediments. To the north, it passes into the eastern syntaxial bend of the Himalayas and southward through Chin-Arakan-Yoma-Andaman-Nicobar into the Mentawai group of islands of the Sumatra coast (Mitchell & McKerrow, 1975).

The Cenozoic sedimentary cover accounts for nearly 95 % of the surface area of Nagaland whereas the rest is occupied by igneous and metamorphic rocks of Mesozoic-Cenozoic age. These display a general NNE-SSW trend with moderate to steep dips towards northwest and southeast. Tectonically, the ophiolite belt is exposed in the main frontal thrust zone of the Alpine-Himalayan tectogen lying along the Indo-Myanmar system (Brunnschweiler, 1966). This Complex occurs only in the eastern part of Nagaland and Manipur.

Rocks ranging from the Lower Disang of Upper Cretaceous to Dihing Group of Upper Pliocene occur within this orogenic belt. The Mesozoic rocks are divided into a continental shelf facies and a geosynclinal facies (Mathur & Evans, 1964). They were deposited during the Late Cretaceous marine transgression, which extended from Manipur till the Shillong Plateau. The shelf facies is confined to the southern margin of the plateau, part of which, extends into Upper Assam, below the Brahmaputra alluvium. The geosynclinal facies extends across the orogenic belt into Myanmar.

Disang Group of rocks, at the base, consist of a thick pile of monotonous argillaceous sediments with thin sandy bands. This Group can be further divided into Lower Disang and Upper Disang. A pronounced unconformity separates the two, marking an orogenic event in the area. This event caused folding and low-grade metamorphism of the Lower Disang sediments and took place during Late Cretaceous. This led to the development of an island arc (Arakan-Chin Genticline; Pascoe, 1959) and caused the shallowing of the sedimentary basin in which the Upper Disang sediments were deposited.

The Lower Disang sediments, intermixed with pelagic chert and limestone were deposited at the western margin of the basin on the easterly subducting Indian plate, while the pelagic sediments were deposited in the deeper part of the basin near the western margin of the Myanmar plate. The different facies were brought together and intermixed when the island collided with the Indian plate and subsequently abducted over it. Ultramafic rocks from the oceanic crust as well as from the upper mantle were abducted with the sediments. Plutonic and volcanic activities continued along with the development of the island arc. The division of the basin into two parts continued at least until the deposition of the Barail sediments during Late Eocene-Oligocene times. While the basin shallowed, northward transgression caused deepening of that part of the basin where the Kopili sediments, mainly argillaceous, were deposited. They are coeval with the Upper Disang and grade into the Upper Eocene-Lower Oligocene Barail sediments.

The Barail rocks consist mainly of thick and coarse arenaceous sediments, coal seams, which indicate increased supply of sediments and shallower water deposition. The shallowing of the basin was linked with the uplift due to the continuing collision of the Indian and Myanmar plates and the increased supply of sediments from the north caused by a recent uplift of the Himalayas. That the Barail sediments were derived from the recently uplifted island arc in the Indo-Myanmar Origen which is indicated by the presence of tuff, volcanic and volcanogenic debris. The sediments were derived from the Arakan-Chin Genticline.

The Patkai-Naga hills were raised above sea level at the end of the Barail times, as indicated by the absence of younger sediments. However, tidal to shallow marine sedimentation continued from upper Assam to the southwest, covering upper Assam, Cachar, western Manipur, Mizoram and Tripura. The succeeding Tipam Formation was fluviatile. The extended area of the Tipams indicates the development of the Himalaya fore-deep in northern Assam during the Miocene when sedimentation extended to the foot of the Himalayas.

An important unconformity separates the Tipam Formation from the overlying Dupitila sediments of Middle Miocene, which suggest upliftment of both the Himalaya and the Indo-Myammar Orogen. Unconformity also separates the Dupitila from the overlying Dihing sediments and the Dihing sediments from the overlying Pleistocene and recent.

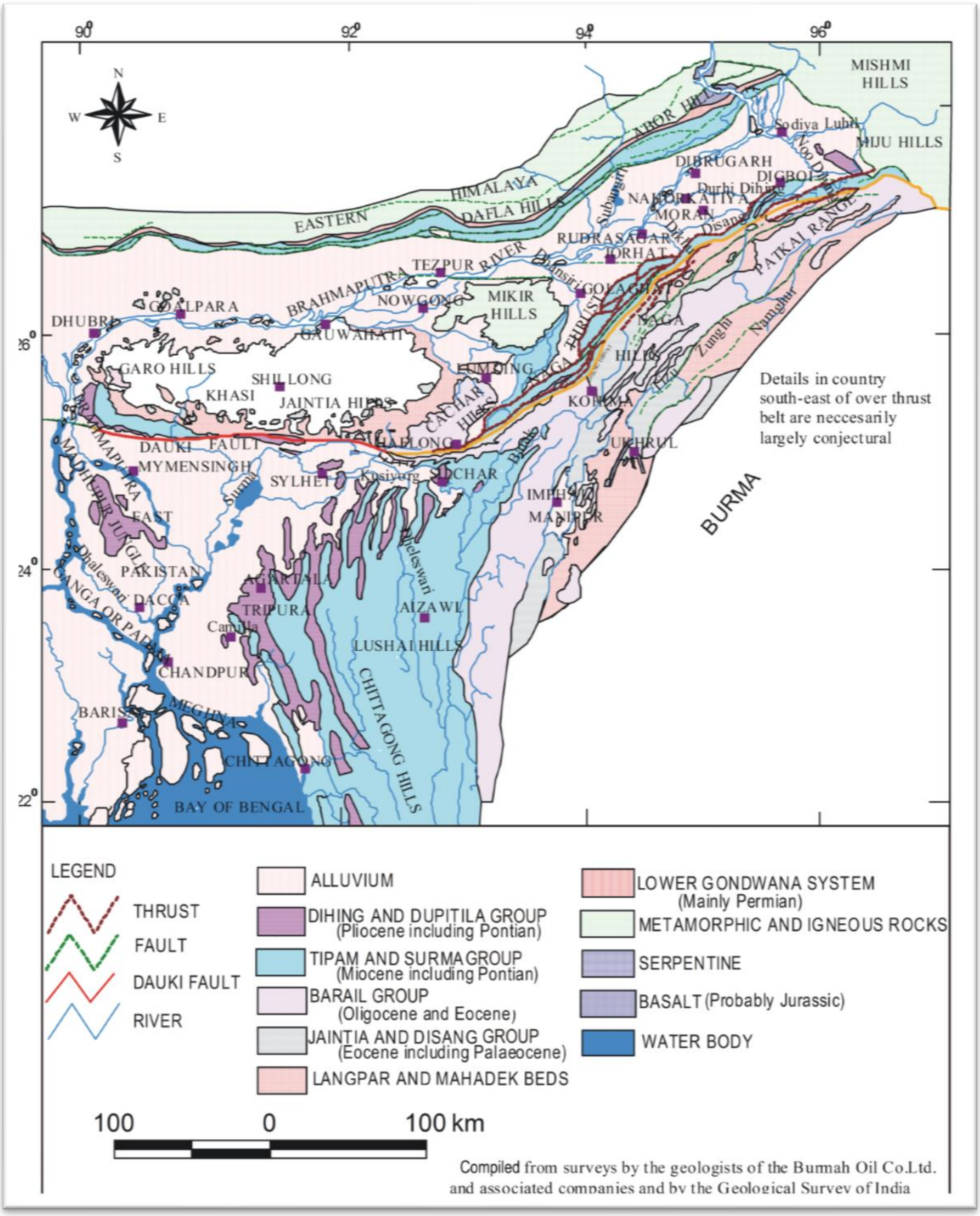

Fig. No. 02. Geological map of various adjoining areas of North East India (After Das Gupta, 1977)

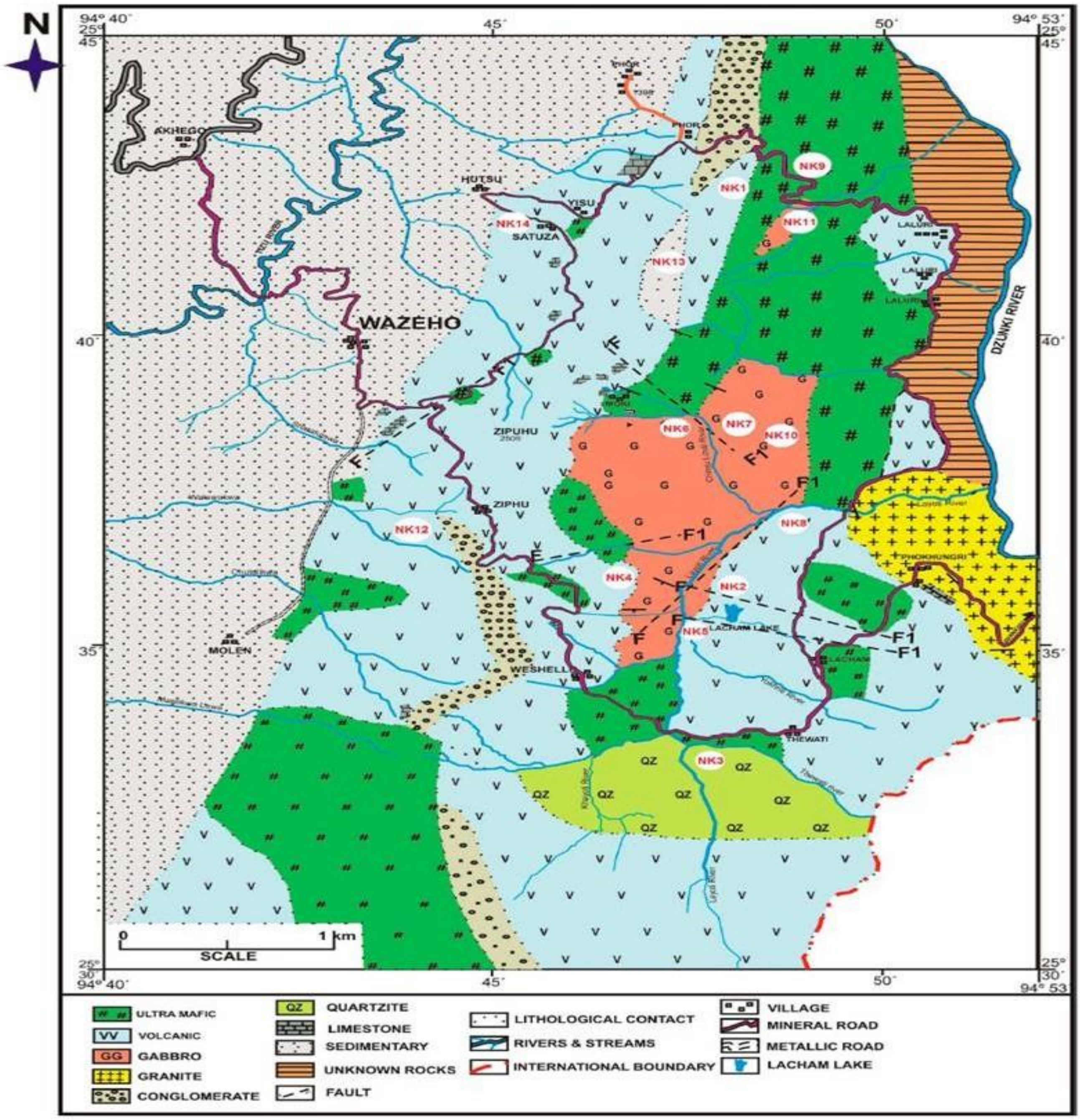

Fig. No. 03. Geological map of various adjoining areas of the study area (After GSI, 2015)

2.1.1 MAJOR STRUCTURES OF NAGALAND

Based on the morpho-tectonic elements, the Naga Hills has been longitudinally divided from west to east, into three distinct units, namely the Belt of Schuppen, the Inner Fold Belt and the Ophiolite Belt.

The Schuppen Belt is a narrow linear belt of imbricate thrust slices which follows the boundary of the Assam valley alluvium for a distance of about 350 km along the flank of the Naga-Patkai hill ranges. It is postulated that this belt comprises eight or possibly more over thrusts along which the Naga Hills has moved north-westwards relative to the foreland spur. The total horizontal movement of all the thrusts together is estimated to be over 200 km. The Schuppen Belt is delineated on the east by the Halflong-Disang Thrust and on the west by the Naga Thrust which has an *en-echelon* disposition. Sediments ranging in age between Eocene-Oligocene and Plio-Oligocene and Plio-Pleistocene along with total absence of Disang rocks together characterize the Schuppen Belt.

The Inner Fold Belt occupies the central part of the Naga Hills and extends up to the Pangsu Pass in Arunachal Pradesh. A large spread of Disang rocks with isolated covers of Barail as well as Disang-Barail transition sequences characterizes the geological settings of the belt. The Palaeogene rocks have been folded into a series of anticlines and synclines and are confined within two major tectonic zones, viz. the Halflong-Disang Thrust to the west and the Ophiolite-Disang contact to the east. The Inner Fold Belt is occupied by two major synclinoria, the Kohima Synclinorium to the south and Patkai Synclinorium to the north, Mokokchung and its adjoining areas being the culmination point of the two. In the Kohima Synclinorium the younger Surmas are developed in the core (Pandey, 2005).

The Ophiolite Belt extends along the eastern margin of Nagaland state for nearly 200 km bordering Myanmar. It is characterised by dismembered tectonic slices of mafic volcanics, mafic & ultramafic cumulates, gabbros, plagiogranites. The associated pelagic sediments include mainly chert and limestone that are often interbedded with the volcanics. The cherts are usually bedded and contain radiolarians. Fossil assemblages from the chert and limestone interbands have suggested an Upper Cretaceous to Lower Eocene age for the Ophiolites. The Ophiolite Suite of rocks are unconformable overlain by ophiolite-derived volcano clastics and open marine to sedimentary cover which have been designated as the Phokphur Formation.

2.1.2 STRATIGRAPHIC SUCCESSION OF NAGALAND

The geological and stratigraphic succession of Nagaland is given in Table-1. The characteristic features of the various Groups and Formations are described in brief as follows:

Nimi Formation: This formation exposed to the east of the NO belt along the Indo-Myanmar border over a stretch of 18x12 km. They probably represent a detached block of the Pre-Tertiary Burmese continental crust. This formation comprises a thick pile of folded meta-sedimentaries which are primarily of a calc-psammopelitic sequence. The main litho-units constitute interbands of phyllites, quartzite, limestone and quartz-sericite schist. An extensive deposit of whitish grey to grey coloured crystalline limestone/ marble is associated with this formation.

Zipu Formation: This is the part of the Ophiolite Complex of Nagaland and lies in between the Nimi Formation and the Disang Group. It shows a linear trend (NE-SW). The rocks include peridotite, serpentinite, gabbro, dunite, volcanics, etc. mixed with oceanic sediments such as chert, greywacke, limestone, etc.

Phokphur Formation: It is named after the Phokphur village in Tuensang district of Nagaland. Based on the faunal assemblages it is considered contemporary to the Disang Group of rocks. It is an Ophiolite derived from volcaniclastic sequence that overlies the dismembered Ophiolite Complex unconformably.

Disang Group: The Disang Group of rocks found first time in the section of Dilli and Disang River was named by Mallet (1876). It is the oldest Tertiary formation of Nagaland and occur in between the Ophiolite complex and the Halflong-Disang Thrust (Das et al, 1977). The Disang is divided into two units viz. Lower and Upper Disang on the basis of degree of compaction. The Lower Disang is made up of shale intercalated with thin flaggy sandstone and contains Cretaceous fauna while the Upper Disang has a proportionately greater volume of sandstone and contains Eocene Nummulites. The Disang Group is interpreted to have been deposited as deep sea fans. The thickness varies between 2000 to over 3000 metres. The Disang Group is interpreted to have been deposited as deep-sea fans. The lower contact of this Group is not exposed whereas it conformably passes upward into the Barail Group. They comprise dark to black carbonaceous and ferruginous concretionary shales with thin beds of siltstone and sandstone.

Barail Group: Barail Group has been named after the Bore-Ali Range in Surma valley, Cachar and forms part of oldest stratigraphical unit till date in the Belt of Schuppen. The Barail Group of rocks are conformably underlined by the Disangs, which comprises of thick sandstone bands intercalated with thin papery shale. The Barails are subdivided into the Laisong, Jenam and Renji Formations in southern and south-western Nagaland and Tikak Parbat, Baragolai and Naogaon Formations in the intermediate hills.

Laisong Formation: it has been named after a village in Cachar is consists of grey, thin to thick bedded sandstones with ferruginous concretions and often possesses intercalations of siltstones and dark grey carbonaceous shales. The thickness varies between 900 and 2000 metres.

Jenam Formation: it has been named after the river Jenam has gradational contacts with the underlying and overlying Laisong and Renji Formations respectively. The rocks are dominantly grey to dark grey with intercalations of carbonaceous shales and siltstone. This formation is characterised by thin to massive bedded sandstones. The thickness varies between 900 and 1200 metres (Pandey, 2005).

Renji Formation: it has been named after the town of Badarpur in Silcharwhich was previously known as Renji. It has a conformable contact with the upper Jenam Formation and is unconformably overlain by the Surma group of rocks. It consists of massive and thick bedded sandstones with minor carbonaceous shale intercalations. The thickness of the formation varies from 700-1000 metres.

Naogaon Formation:has been named after the village Naogaon, shows a gradational contact with the overlying Baragoloi Formation. The rocks of this Formation are characterised by interbedded sandstone and shale. The thickness varies between 800-1000 metres.

Baragolai Formation: Lower and Upper contacts are gradational with the Naogaon and Tikak Parbat Formations. It comprises of interbedded sandstone and shale with distinct coal seams. The thickness varies from 2500-3000 metres.

Tikak Parbat Formation has a gradational contact with the lower Baragolai Formation while its upper contact with the Surma/ Tipam Groups is unconformable. It comprises of a sequence of sand-shale alternations with thick coal seams. The thickness varies between 170-700 metres. The Laisong, Jenam and Renji Formations of the Barail Group of rocks are well developed in the southern part of the Schuppen belt while the other division i.e. Naogaon, Baragolai and Tikak Parbat Formations are seen towards the northern part of the belt.

Jopi Formation is considered to be equivalent of the Barail. They are unconformably overlain the Ophiolite suite of rocks occupying at different topographic levels. It consists of a thick pile of alternating and repeated sequence of polymictic conglomerate-grit-pebbly and cobble sandstones, sub greywacke and shales. The individual cycles varies in thickness from less than a metre to over 10 metres, the overall thickness of the formation being more than 600 metres.

The basal conglomerate unit contains angular to sub-rounded boulders, cobbles and pebbles. They derived from the underlying Ophiolite suite and embedded in a reworked tuffaceous/ siliceous cement. The succession grades upward into grit, lithic greywacke, siltstone and shale. The sandstones gradually become arkosic towards the top.

Surma Group: The Surma Group of rocks is exposed in the core of the Kohima Synclinorium within the Belt of Schuppen. In Nagaland the two divisions of Surma Group, i.e. Bokabil and Bhuban formation but cannot be differentiated. As a whole alternating succession of grey laminated shale, sand and conglomerate comprise the Surma rocks in Nagaland. The overall thickness varies between 300-800 meters. The Surma Group, a molasse facies of Lower Miocene age, lie unconformably above the Barail Group.

Tipam Group: The Tipam series was first named by Mallet (1876) after the Tipam Hill between DihingRiver and Digboi in Upper Assam. Both Lower Tipam sandstone and Upper Girujan Clay Formations are present in the Belt of Schuppen of Nagaland. The Tipam sandstones overlie conformably the Surma rocks and are characterized by multi-storeyed, channelled, false bedded, coarse to medium-grained arkosic soft sandstones. Minor intercalations of fine sandstones-silt-mud can also be seen at places. On the other hand, the Girujan Clay Formation is dominated by thick sequences of mottled and variegated clays with a few silt and sand intercalations.

Namsang Formation: The Namsang Formation was first referred by Evans (1932) from its types in Namsang River. They are unconformably overlain by the Tipam Group. These rocks belong to the Dupitila Group. These consist of blue to bluish grey clays with intercalated silts and sands. The thickness varies between 400-1080 metres.

Dihing Formation: The name was first designated by Mallet (1876) to a group of pebble beds exposed in the Dihing River of Upper Assam. Dihing Formation is well developed in Nagaland along the western margin of the Belt of Schuppen. They consist mainly of thick pebble beds with clays and soft sands resting unconformably on the Tipam Group and Namsang Beds. They occur in a few patches in the western margin of the Belt of Schuppen.

Alluvium and High-Level Terraces: Alluvium and High-Level Terraces cover small portions of Nagaland. The terraces are dominantly boulder beds with coarse sands, gravels and unsorted clays. They occur at various levels above the present rivers. The older alluvium occupies the north eastern tract of the Naga-Patkai range while the newer alluvium covers the western border of Nagaland.

Age	Belt of Schuppen			Disang Group			Ophiolite Belt
Quaternary	Alluvium and high level terraces			Alluvium and high level terraces			Alluvium and high level terraces
Pliocene- Pleistocene	Upper Dupi Tila Dihing Namsang			--------------			--------------
---Unconformity---							
Mio-Pliocene	Tipam (2300)	Girujan Tipam sandstone Formation					
	Surma (+1250)	Bokabil Upper Bhuban Middle Bhuban		Upper Bhuban (1850) Lower Bhuban (1000)			
--- Unconformity---							
Oligocene to Upper Eocene	Barail	Tikak Parbat (620) Baragolai (2720) Naogaon (+1400)	Renji (900) Jenam (+830) Laisong (+1750)	Barail (Undifferentiated)			Jopi formation (=Phokphur formation =Lower Barails (?)
---Gradational contact---Unconformity-----------------------------------							
Eocene	Jaintia						
Upper Cretaceous to Upper Eocene				Disang (> 3000)	Upper Disang Lower Disang	Disangs (Lower Disang?) Tectonic contact	Ophiolites (=Late felsic intrusives, Pelagic-volcanogenic sediments, volcanics, Metabasic, Meta-acidites, Cumulate Mafic-ultramafics and metaultramafics
						------------------- Tectonic contact---------------	
Mesozoic (?)	----			----			Nimi Formation (Metamorphics)
	-----------------------------------Unconformity-------------------------------						
Precambrian	Mikir Hills Massif			??			??

Table No. 01: Stratigraphic succession in Nagaland (modified after Ghose *et al*, 1986)

2.2 LOCAL GEOLOGY

The Naga Ophiolite Belt occurring along the Indo-Myanmar border forms a part of the Naga-Arakan-Yoma flysch trough of Upper Cretaceous–Middle Miocene age. This belt is tectonically sandwiched between the Nimi Formation on the east and the Disang flysch towards the west. The NOB, extending over 90 km in length along the strike with widths varying from 2-15 km, covers an area of about 1000 sq. km. The Indo-Myanmar Range (IMR) is considered the northern prolongation of the Indonesian Island Arc, which in turn is linked up northward with the eastern end of the Himalayas (Acharyya *et al*, 1986).

The ophiolites in the N-E corner of India are drifting and of various dimensions, floating in a matrix. They consist of a various mixture of igneous, sedimentary and metamorphic rocks of which the mafic and ultramafics are the main components. They do not constitute a continuous sheet but are made up of units randomly juxtaposed along faults or they consist of lensoid slices inter-bedded with the Disang Group of rocks (Bhattacharjee, 1991).

There is a shallow water sedimentary cover consisting of conglomerate, sandstone, shale and phyllite over the ophiolites. The main litho-members are shale, phyllite, slate, greywacke and sub-greywacke within the Disang flysch belt. The metamorphic belt consists of a variety of low grade meta-sediments such as quartzite, meta-greywackes, limestone and phyllite with other members of the ophiolite, mainly serpentinite and volcanics. A sequence of limestone-shale occurs as pockets and lenses close to the Disang sediments which have a tectonic contact with the Disang Formation.

The Nagaland Ophiolites are mainly represented by (1) Mafic Volcanic (2) Ultramafics (peridotites, pyroxenites, serpentinites) (3) mafic cumulates (gabbros) (4) Plagiogranites, (5) Glaucophane-schists, (6) Amphibolites, (7) Associated sediments consist of chert, shales and limestone (Fig.4). All these varieties may occur in close association in the similar exposure. Fine veins of calcite are found in the ultramafics.

The ultramafics are the predominant rock type of the Ophiolite complexes. They are well exposed along the entire length of the belt. Limestone in faulted contacts with Disang shales are identified as exotics.

In the Naga Ophiolite Belt, there are large numbers of limestone bands of variable dimensions and these could be broadly grouped into the following Stratigraphic categories:

i. Limestone occurring as tectonic slices in Disang Formation within the Ophiolite: near the contact with the ophiolites, towards the west, there are only minor limestone bands within the Disang. A medium-sized limestone deposit has been recognized near Hundung by the GSI. The two other known occurrences are in Nagaland are towards Meluri from Pfutsero, where the Disang is composed of shale, slate, sandstone and thin bands of limestone and the other being located about 2 km. west of Kiphire are two pockets of limestone within the Disang shale. It is grey and pink coloured, argillaceous in nature and extends over 115m with thickness varying from 7m-10m (Singh, 1978).

ii. Limestone associated with volcanic chert of the Ophiolite suite:

Limestone of this category is often closely interbedded with chert- volcanic assemblage. The following are some of the localities that reported such type:

a. Shatüza- Yisi: limestone bodies of variable dimensions occur in these localities associated with chert and fine grained volcanic, as lenses, bands and pods arranged ‘en enchelon’ parallel to the formation of the basic rocks. They are white to grey crystalline limestone with similar scent of sulphuric acid on fresh surface.
b. Mokie: there are a few N-S trending white coloured limestone bands with strike length varying from 50 m to 100 m. Three medium- sized lensoid bodies which occur within spilite and chert are similar in physical and chemical characters to that of Wazeho- Satuza deposits.
c. Wazeho: in this area there are several steeply dipping lenticular pockets of limestone of varying dimension within an area of 0.5 sq. km. This occurrence is adjacent to the contact with the Disang Formation and located SSE of Wazeho village in the western margin of Zepuhu range (2509 m). The biggest

of these pockets is about 700 m x 10 m to 50 m x 50 m in size and exposed as a tectonic contact with chert.

iii. Limestone associated with phyllite- quartzite and other metamorphic and forms part of the Naga Metamorphics (Nimi Formation):

In this category, there are quite a few occurrences most of which contain thin partings of phyllite-quartzite. Some of the occurrences examined are as follows:

a. Laruri: non-crystalline, well bedded limestone is exposed within shale-slate-sandstone units at about 2 km NE of the Laruri village. A cave in this band, with development of stalactite and stalagmite is observed. The bands are folded, fractured showing minor slips (Srivastava et. al, 1983).
b. Phokhungri: in the Phokhungri- Thewati track, ash coloured massive grey limestone band is exposed trending N2˚E- S2˚W with 75˚ dip towards west. The dimension of the deposit is 300 mx 75 m.
c. Thewati: There are a few ash coloured limestone bands in this area with thin partings of phyllite forming scarp face. In addition to that two lensoid bodies having approximate dimension of 120 m x 40 m each found at east of New Thewati. Another band measuring 750 m x 25 m occurs near Old Thewati. Along strike direction of this band is another band measuring 120 m x 20 m.

The generalized fourfold classification (**Table No. 02.**) of the litho units has been built up for the Ophiolite and Metamorphic Complex of the eastern parts of Phek and Tuensang Districts of Nagaland is given below (Rao and Kikon, 1985).

Age (approx.)		Litho members
Late Palaeogene		conglomerate, sandstone, greywacke and shale.
------------------------------Unconformity--		
Upper Cretaceous to Eocene.	Disang Flysch	shale,slate, phyllite, greywacke, minor limestone brine springs.
------------------------- Tectonic contact---		
Emplaced during Eocene	Ophiolite complex	meta-ultramafic, peridotite, pyroxenite, basalt, spilite, gabbro, basic-schist, blue-schist, chert, limestone, phyllite, etc.
-------------------------- Tectonic contact---		
Palaeozoic (?)	Metamorphic	quartzite, Phyllite, limestone meta-greywacke, tectonic slices of Ophiolite.

Table No. 02. Fourfold classification of Litho Units of Nagaland (Rao and Kikon, 1985)

2.3 TECTONIC SETTING:

The NO Belt relates to the oblique subduction and subsequent collision between India and the central eastern Burmese continental blocks during the Upper Cretaceous-Eocene. A linear arcuate deep basin developed along the leading edge of the subducting Indian plate in which the Disang sediments were deposited. The Disang Group of rocks, representing the accretionary prism and the associated sediments deposited at the subduction, end in the east. The Myanmar volcanics and the Ophiolite Belt seem to have supplied the source material.

The arcuate NO belt bordering Myanmar in the northern part of the Indo-MyanmarRange is considered to be linked with those of the Andaman & Nicobar-Sunda Arc System and the Alpine-Himalayan mobile belt. In recent years, various tectonic models involving two major suture zones bordering India have been proposed viz. the Indus Suture Zone and Naga Arakan-Yoma Suture Zone though not much basic geological data are available, except few (Acharyya, 1986). It is thus tempting to agree with the observation that hard data about the Indo-Burman arc are still too scanty to justify many published tectonic syntheses (Brunnschweiler, 1983).

The belt has a linear NNE-SSW to NW-SE disposition and is bounded by longitudinal lineaments parallel to the trend of the orogenic belt. Three phases of folding have affected the sediments. These movements are probably related to local thrusting and the upliftment of the Mio-Pliocene sediments forming horst and graben-like structures in the Indo-Myanmar ranges and the Central Lowlands of Myanmar. This narrow tectonised Ophiolite Belt is believed to represent the remnants of the Tethyan oceanic crust which was largely sub ducted resulting in the collision of the Indo-Australian plate with the Eurasian and Sundra plates (Acharyya et al, 1986).

Recent geological investigation by the GSI has led to the synthesis of the regional framework of the NO Belt (Acharyya et al, 1984; GSI, 1986). It is recognized that the oceanic crust preserved as ophiolites might have been produced in diverse tectonic settings (Coish and Church, 1979; Coleman, 1981; Gass, 1982; Schmincke et al, 1983).

In conclusion, it may be stated that the Indo-Burman orogenic belt formed due to the collision of the Indian plate with an island arc and then collision of the Indian plate welded to the island arc with the Burma plate. The subduction of the Indian plate under that of the Burmese initiated during the Cretaceous has perhaps continued to the present time (Bhattacharjee, 1991)

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CHAPTER- III

METHODOLOGY

3.1 INTRODUCTION

In the present study, various field and laboratory techniques have been adopted to decipher the physical, optical and chemical properties of the limestones and associated rocks. The methodology and instrumentation techniques used are described in this chapter.

3.2 FIELD TECHNIQUES

Reconnaissance surveys were made and the outcrops of the limestones and associated rocks were selected for study during the course of fieldwork. The study area includes several sectors and traverses were made across the limestones and associated rocks. Detailed field investigation had been carried out in Wazeho, Shatüza, Laruri, Phokhungri, New Thewati, Zhipu and Mokie villages of Phek District, Nagaland during field seasons (years) of 2017-18 and 2018-19. The area of investigation is about 438 sq. km has been geologically mapped on a scale of 1:50,000. Most of the terrains are inaccessible for which field works happened to be a challenging task. The location of the rocks was taken with help of GPS and also used Brunton compass and then plotted in the toposheet.

Field data includes location and inter-relationships of various litho types and structures (strike, dips of foliation, faults, joints, lithological boundaries and textures are noted in the field with the help of traditional geological tools (toposheet, Brunton compass, hand lens, measuring tape, hammer and note book etc). About 120 rock representative samples of limestones and their associated rocks were collected from various localities of the study area for petrography and geochemical studies. Field photographs and sketches are taken, wherever necessary, in the field.

3.3 LABORATORY STUDIES

Laboratory work adopted in the present study includes the preparation of rock thin sections (about 60 rocks) for optical studies and powder for geochemical analyses. Optical studies were carried out at the Department of Geology, Nagaland University with a Nikon Polarizing Microscope (Model Pol-400).

Geochemical studies were carried out at the Geochemistry Division, NGRI, Hyderabad for estimation of major, trace and rare earth elements by using X-Ray Fluorescence (XRF) Spectrometry and Inductively Coupled Plasma-Mass Spectrometry methods (ICP-MS).

3.3.1 Sample preparation for thin sections

Based on physical characters and distribution of rock types, representative limestones and their associated rocks have selected for the preparation of thin sections. For the study of thin sections under the Petrological microscope rock, slides from fresh rock chips were prepared using conventional methods of rock cutting and polishing with different sizes of carborundum powder.

3.3.2 Preparation of powder for geochemical analyses

For rock analyses, small fresh pieces of 1 to 2 cm sized chips are obtained from each specimen by hammering on a steel anvil. The rock pieces are crushed and ground to pass through a -100 mesh and in the case of mineral separation and through a -170 mesh for rock analysis.

While powdering the samples, precaution was taken as much as possible to avoid contamination after processing each successive sample. After every sample is crushed and grinded, the steel mortar as well as the agate mortar was thoroughly cleaned by isopropyl alcohol.

3.4 OPTICAL STUDIES

About 50 thin sections of rocks are studied. Optical studies were carried for the identification of rocks and their mineral assemblages, modal mineral composition, textures, transformation and effects of metamorphism. Pleochroism Scheme and absorption formula are recorded by orienting the mineral grains on the U-stage. The refractive indices are determined by the inversion methods and the refractive index of the liquid is immediately determined on Jelly's and Abbee's Refractometer under Sodium light at 25º. The various optical properties of each mineral, such as colour, habit, textures, relationship with other minerals etc. are studied under plane-polarized light as well as between cross polars. Important characters of minerals and their relationships are photographed.

3.5 ANALYTICAL METHODS

Rock chips are crushed in tungsten carbide (TC) in the Herzog Grinder Set and finally ground to a very fine powder using an agate mortar and pestle. The finely powdered samples passing through a -300 mesh are used for the geochemical analyses for estimation of major, trace and rare earth elements by using X-Ray Fluorescence (XRF) Spectrometry and Inductively Coupled Plasma-Mass Spectrometry methods (ICP-MS).

3.5.1 X-Ray Fluorescence Spectroscopy (XRF)

X-ray fluorescence (XRF) spectroscopy is an instrument used for determination of major elemental concentrations of a substance. An element is identified by its characteristic X-ray emissions. The quantification occurs by measuring the intensity of the characteristic emission line(s).

The XRF method is widely used to measure the elemental composition of materials (rocks and minerals). Since this method is fast and non-destructive to the sample, it is the method of choice for field applications and industrial production for control of materials. Depending on the application, XRF can be produced by using not only x-rays but also other primary excitation sources like alpha particles, protons or high-energy electron beams.

In XRF spectrometry, a high-energy X-ray photon is emitted from an X-ray source and strikes the sample. High energy X-ray photons have sufficient energy to remove electrons from the innermost K or L orbitals. When this occurs, the atoms become ions, since a negative charged electron has been removed. These ions are unstable. To return to a more stable electronic arrangement, electrons from an outer orbital, like L or M, move into the newly vacant inner orbital. In this process of an electron, moving from an outer to an inner orbital an X-ray photon is emitted. This photon is termed a secondary X-ray photon, in contrast to the primary X-ray that was emitted from the X-ray source. This phenomenon of electrons moving from outer to inner orbitals with a corresponding emission of photons is called fluorescence. The energy of the emitted fluorescent X-ray photon is dependent on the differences in energies between the initial and final orbitals of the individual transitions. Importantly, the secondary X-rays produced in this process are characteristic of a specific element. In other words, we can identify the elements present in a sample by analyzing the energy of the secondary X-rays.

A constraint of X-ray fluorescence spectroscopy is that it is not generally suitable for analyzing light elements. The X-ray fluorescence spectrometer will not be able to analyze elements with an atomic number below 19 (potassium). This may be viewed as a limitation, since the spectrometer is unable to identify common elements like aluminium or silicon in a sample. It is also unable to identify species like acetate. However, a positive feature is that many sample holders that are made of organic polymers (primarily C, H, O) will be transparent for both primary and secondary X-ray photons. This means that the sample to be analyzed can be placed in a material transparent to X-rays, like a plastic bag, and analyzed directly.

The major elements are determined quantitatively by the XRF method. A total of 20 representative rock samples are finely powdered with the help of Jaw Crusher and Pulverizer. Pressed pellets (Briquette) are used for the analysis. The pressed pellets are prepared by using collapsible aluminium cups. These cups are filled with boric acid and about 1 gm of the finely powdered rock sample is put on top of the boric acid and pressed under a hydraulic press at 20 tons of pressure to obtain one pellet. To make more stable and durable pellets some binders like wax, starch, cellulose or other organic compounds are added to the rock sample. The mixture is thoroughly mixed and pressed in a hydraulic press.

3.5.2 Inductively Coupled Plasma Mass Spectrometry Analysis

Inductively Coupled Plasma Mass Spectrometry or ICP-MS is an analytical technique used for elemental determinations. The technique was commercially introduced in 1983 and has gained general acceptance in many types of laboratories. Geochemical analysis labs were early adopters of ICP-MS technology because of its superior detection capabilities, particularly for the Rare Earth Elements (REE). ICP-MS has many advantages over other elemental analysis techniques such as atomic absorption and optical emission spectrometry, including ICP Atomic Emission Spectroscopy (ICP-AES), including:

- Detection limits for most elements equal to or better than those obtained by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS).
- Higher throughput than GFAAS
- The ability to handle both simple and complex matrices with a minimum of matrix interferences due to the high-temperature of the ICP source
- Superior detection capability to ICP-AES with the same sample throughput
- The ability to obtain isotopic information

ICP-MS is best used for simultaneous multi-element determination of trace and REE in various geochemical materials. Trace elements and rare earth elements (ppm) are analysed using an ICP-MS Model ELAN DRC II (Perkin-Elmer instrument, US). The open acid digestion method was adopted. For analysis, 50 mg of powdered samples are taken in PTFE Teflon beakers. Each sample is moistened with a few drops of water. Then a mixture of 7:3:1 (7 ml of HF, 3 ml of HNO_3 and 1 ml of $HClO_4$ /HCl) is added to each beaker and the sample is swirled until completely wetted. Beakers are then covered with lids and kept overnight for digestion. Next day the beakers are heated on hot plates at 200º to 250ºC for about 1 hour after which the lids are removed and the contents evaporated almost to dryness. The evaporation process is repeated twice after adding a mixture of 5 ml in the ratio of 7:3:1 in each case. Then the contents are dissolved using 20 ml of 1:1 HNO_3 and 5 ml of Rh that act as internal standards then the volume is made to 250 ml and stored in polythene reagent bottles; clear solutions are obtained in all cases. This gives a dilution of 1:1000. The solutions are used to determine the trace and rare earth elements.

3.5.3 Petrochemical calculations and graphical diagrams

The chemical data obtained have been processed through a number of petrochemical calculations and their graphical representations including various bivariate diagrams of major oxides, trace and REE for the analysed samples made to unravel the genesis and economic viability of limestones.

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CHAPTER IV

FIELD RELATIONS AND PETROGRAPHY

4.1 INTRODUCTION

The Earth is composed of a large variety of rocks, which were created and evolved. The Ophiolite suite of rocks of the study area are studied on the basis of mode of occurrence, lithological association and field relationships. Petrographic examination provides most valuable petrogenetic information of the rocks. The textural features of rocks are record of rock forming processes “written in the stone” (Hibbard, 1995). Petrographic characterisation of NOB samples starts with the field notes of the outcrop, which include megascopic description of hand specimens. However, the most important tool for the researcher is the petrological_microscope. The detailed analysis of minerals by optical study in thin sections, the micro-texture and structure are crucial in understanding the origin of the rock.

Careful petrographic observation in thin-section is a must for meaningful interpretations of rocks in re-constructing their petrographic histories and petrogenesis. Minerals found in the rock reveal enigmatic messages from their textures and relations with other associated minerals in the rocks. And hence, petrography reveals the magmatic processes involved and the paragenetic sequences of the rocks.

The Magmatic textures are also considered useful indicators of cooling, crystallization rates and phase relations between minerals and magma during its crystallization process. Ultimately, the field and petrographic observations help us to interpret and reconstruct petrographic history and petrogenesis.

4.2 FIELD RELATIONS

The Ophiolite Belt in the eastern part of Nagaland is an arcuate linear belt between the Disang flysch on its west and Nimi Formation (metamorphics) on its east, extending for a strike length of 90 km with varying width of 2 to 15 km and covers an area of about 1000 sq. km. Fault–bounded slices observed in most of the major rock units. Primary contacts are well exposed along the road sections, and it is often concealed beneath the scree cover. More often, blocks of various sizes and types are juxtaposed against each other along irregular, sheared contacts.

The Ophiolites of northeast India are rootless blocks of various dimensions, floating in a matrix, which belongs to the Upper Cretaceous–Lower Tertiary Disang Group. They consist of diverse igneous, sedimentary and metamorphic rocks, of which ultramafics are the main component. They do not constitute a continuous sheet but are made up of units randomly juxtaposed along faults or they consist of lensoid slices inter bedded with Disang Group rocks (Bhattacharjee, 1991).

The following major lithological units have been identified in the Naga Ophilite Belt based on the field relations (Table No. 02):

1. Ultramafic complex : (a) Tectonised peridotites, (b) ultramafic cumulates.
2. Mafic Cumulates: Gabbros
3. Mafic volcanic complex (Basalt and spilites)
4. Plagiogranites and granites
5. Associated sediments : Cherts, limestones and conglamerate etc.

Although the limestone comes under associated sediments, it has an enormous deposit that no other rock types could match this huge deposit. The major limestone deposits are exposed at are Wazeho, Shatüza, Laruri, Phokhungri, New Thewati, Zhipu and Mokie of Phek District, Nagaland. They differ largely in colour, texture, hardness and durability from one place to another. The colour of limestone is white, greyish white, grey, greyish blue to steel grey. Most of the deposits are massive and the rock was affected by tectonic activities. The occurrences of limestones are discussed below as per field observations:

4.2.1 Wazeho Area

The Limestone deposits found in and around Wazeho and is in tectonic contact with the Disangs on its West. The limestone deposits spread over an area of around 0.5 km. It occurs in linear fashion having a length of 570m, and thickness varying from 5m - 20m.The associated rock types in the area are phyllite, chert, mafic volcanics and minor serpentinites. These have a general NE-SW strike and dip to Northwest.

4.2.2 Shatüza

Number of limestone pockets have been noted in the S, SE and east of the Shatuza village and are scattered over an area about 5km to the S- SE and East of the village. This particular ridge originates at a distance of about 1½km ENE of Shatiiza village and extends nearly 4km and finally merges with North peak of Zepuhu range. Altogether eight numbers of detached limestone pockets have been located all along the length of the above ridge from North to South. Of these eight pockets, five located along the ridge from North to South. The remaining three pockets lies outside the area. All the seven pockets are numbered as 1 to 7 and they together are termed as "Shatiiza Limestone Deposit." It occurs in NE strike continuation of the Wazeho deposit. The limestone pockets are associated with Volcanics, Serpentinite and Chert. Some deposits found as an irregularly elongated body on the northern, eastern and southwestern side with a narrow joint at the Centre covering an area of .10 sq.km occurring in association with volcanic and chert towards the SE side of the deposit.

4.2.3 Phokhungri

The deposits are found in the form of rootless pockets at Phokhungri area which are associated with Black marbles. They are fine grained and whitish to grayish in colour with shades of dark bands and shows physical contact with Black marble. The sampled area is locally named as "Lüpzadi Xhang."

4.2.4 New Thewati

A lensoid body of ash colored Limestone deposit is found in the East of New Thewati along the Indo- Myanmar border. They are fine grained, hard, compact and crystalline in nature. The sampled area is traditionally named as "Tsekhong."

4.2.5. Zhipu

The Limestone occur as a drifting deposit along Zhipu- Moke road. They are white, very fine grained and crystalline in nature. Number of Limestone pockets are also located at Zepuhu range, situated at Northern part of Zhipu Village. The sampled area is locally named as "Dhüyamüku."

4.2.6 Mokie

The deposit found at Shakharu- tü is an exotic huge block which is crystalline in nature. They are dark grayish in colour and shows a contact with serpentinite. The limestone deposits occur in the form of detached pockets are scattered over an area of about 2.5 sq. km, with the association of ultramafics and volcanics. Altogether seven numbers of pockets were record on the N-W and SW and SE of Mokie. Out of these, the pocket located 1.5km Northwest of Mokie is considered to be the main band/pocket. Development of fractures, joints is filled with calcite veins, which are common in this area. In general, they are white, whitish grey to dark grey in color, hard massive, compact and crystalline in nature. Some of the Limestone deposits of Phokhungri and Mokie shows physical contact with black marble and serpentinite. The associated rock types are mostly mafic volcanics, phyllite, chert etc.

Plate No. 01- The Black and White Limestone deposits occur along Zhipu- Mokie road

Plate No. 02- The rootless pockets of Blackened limestone found at Lüpzadi Xhaün, Phokhungri

Plate No. 03- A lensoid body of ash colored crystalline Limestone located in the East of New Thewati, Phek District

Plate No. 04- The deposit found at Shakharu- tü, Mokie is an exotic huge crystalline block, dark grayish in colour and shows a contact with serpentinite

Plate No. 05- A limestone deposit at Wazeho, are mostly whitish to ash grey, fine to medium grained, hard, compact and crystalline in nature

4. 3 PETROGRAPHY

Petrographic descriptions start with the field notes at the outcrop and include megascopic description of hand specimens. However, the most important tool for the petrographer is the petrographic microscope. The detailed analysis of minerals by optical mineralogy in thin section and the micro-texture and structure are critical to understanding the origin of the rock.

4.3.1 Megascopic Observation:

The limestones deposits found in the form of detached, rootless pockets/lenses, boulder, bedded and massive type and exotic in nature in the study area. They are hard, compact and crystalline in nature medium to fine grained. The limestone exhibit whitish to ash grey with shades of dark color. Limestone, which had undergone metamorphism, had turned into marble grade at places.

4.3.2 Microscopic Observation:

The limestones mostly vary in colour from greyish white to grey. Petrographic studies affirm that the limestones are mostly composed of calcite with minor presence of dolomite, diopside, chlorite, quartz, and apatite. The calcite grains shows the usual change of relief, which is referred to as "Twinkling" and the colorless calcite grains are seen with irregular boundary, indicating the rocks to have undergone recrystallization. Calcite shows prominent twinning under crossed polar which is to be considered useful in distinguishing calcite from dolomite. The sub-hedral calcite grains showing perfect rhombohedral cleavage (usually in 3 sets) and also observed under crossed polar. Minute crystals of apatite and chlorite are occasionally scattered with fracture planes filled with calcite veins. The following minerals as observed under petrological microscope is described below:

Calcite: It occurs as fine to medium aggregates, usually subhedral in shape. It is colourless or white –may have shades of various colours in thin section and shows perfect three set rhombohedral cleavage, extreme birefringence, extinction symmetrical to the cleavage and polysynthetic twinning. Calcite can be identified in thin section by its rhombohedral cleavage and very interference colours, often so high as to appear almost white, superficially similar to a low interference colour but with little rainbow flashes of colour here and there in the mineral.

Dolomite: is an anhydrous carbonate mineral composed of calcium magnesium carbonate. Dolomite occurs as tabular crystals, often with curved faces, also columnar granular and massive. It shows white, grey to pink reddish white, brownish white ,colourless in in transmitted light, 3 directions of cleavage not at right angles. Common as simple contact twins. Under a microscope dolomite and calcite look similar, but thin sections can be etched and stained in order to identify the minerals. Photography of a thin section in cross and plane polarised light; the brighter mineral grains in the picture are dolomite and the darker grains are calcite.

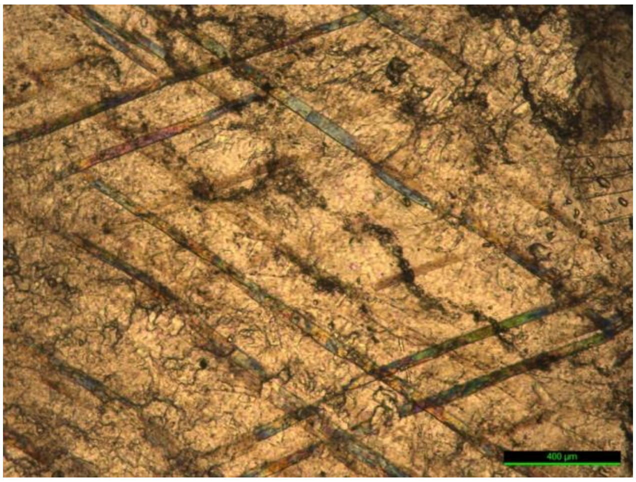
Diopside: it is monoclinic pyroxene mineral and occurs as short prismatic crystals common, may be granular, columnar nature.it forms variable coloured like green, block, yellow and brown. It has distinct prismatic cleavage.

Chlorite: It frequently occurs as flakes with anomalous birefringence and greenish pleochroism. In thin section chlorite appears either as radiating aggregates filling cavities or as alteration products of minerals such as biotite, etc. Cleavage is seen; lamellar twinning and moderate refractive index are recorded; polarization colours are usually ultra-blue and ultra-brown.

Quartz: Quartz is almost absent in some samples. They are anhedral in shape and belongs to two generations: the earlier one occurs as small anhedral grains within and in between feldspar grain boundaries. The latter, which is larger in dimension, encloses un-corroded euhedral plagioclase laths.

Apatite: is a group of phosphate minerals, usually hydroxyapatite, fluora-patite, chlorapatite and occurs as tabular, prismatic crystals, massive, compact or granular, transparent to translucent, usually green, less often colourless, yellow, brown in colour, indistinct cleavage, pink, double refractive, uniaxial negative. Pleochroism is blue stones-strong, blue and yellow to colourless

Opaque (Iron): Iron minerals are common in most igneous and sedimentary rocks. They are late magmatic minerals. Iron occurs as dust and anhedral grains. The grains usually occur along the borders of other minerals. Magnetite is black in colour with a metallic lustre in reflected light whereas hematite is steel grey to black with a tendency to a marginal red; some are red and translucent.



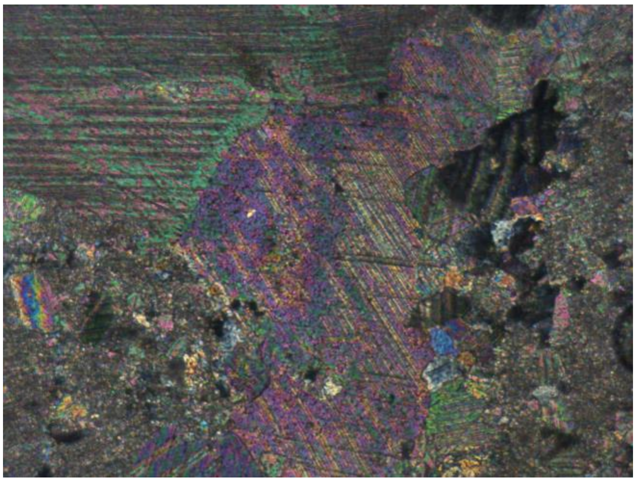


Plate No. 06 **Plate No. 07**

Plate No. 06- Twin lamellae in calcite seen under crossed polars

Plate No. 07- Calcite grains under crossed polar showing irregular boundary

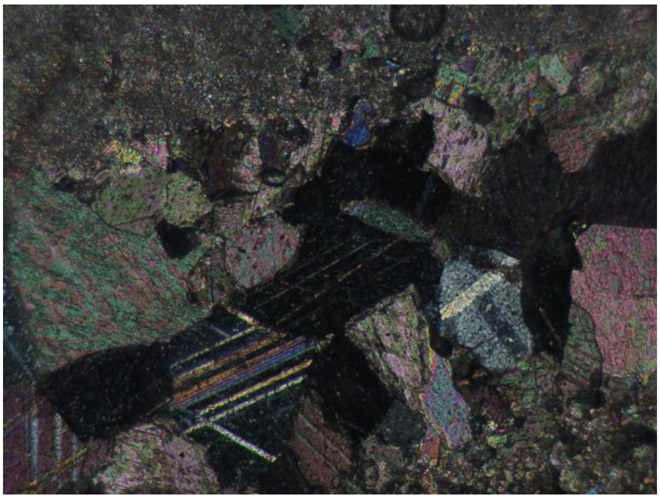


Plate No. 08

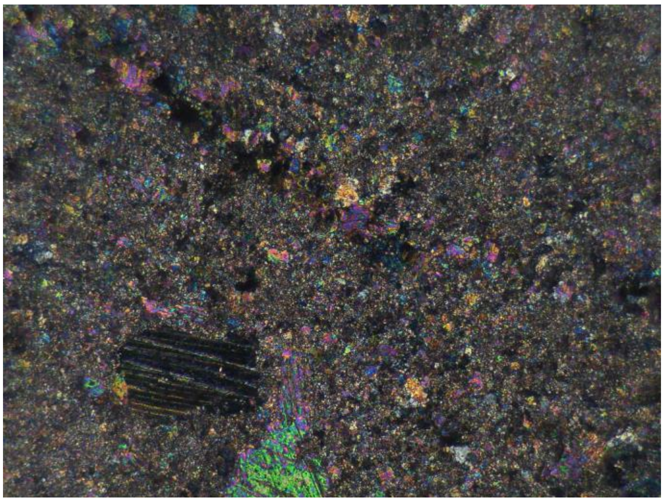


Plate No. 09

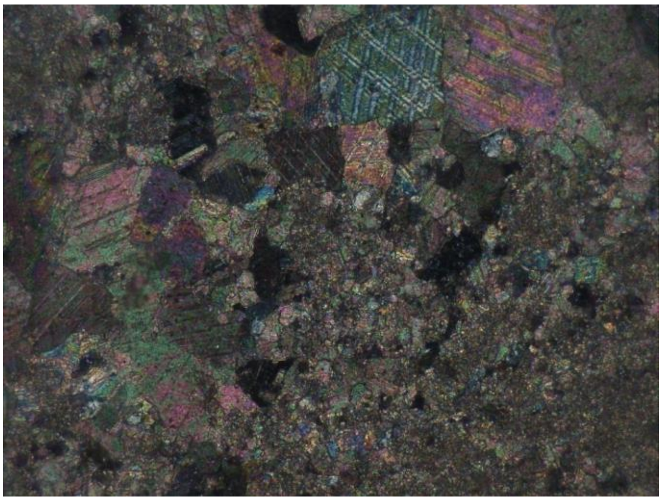


Plate No. 10a

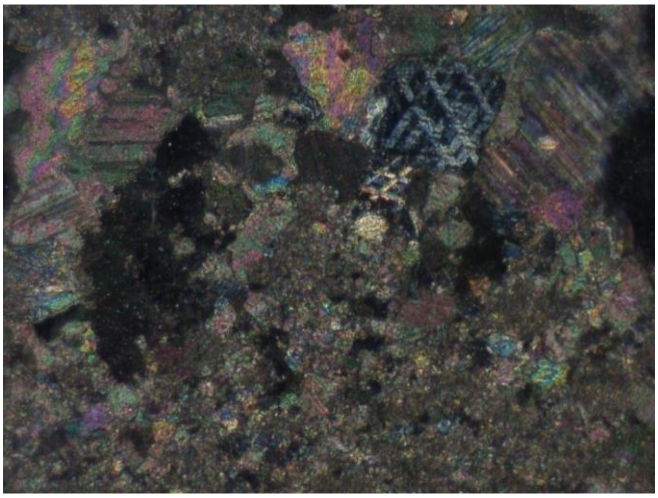


Plate No. 10b

Plate No. 08- Calcite and dolomite dominant with minor amount of chlorite

Plate No. 09- Calcite under crossed polar with minor amount of apatite

Plate No. 10a & 10b- Calcite showing perfect rhombohedral cleavage

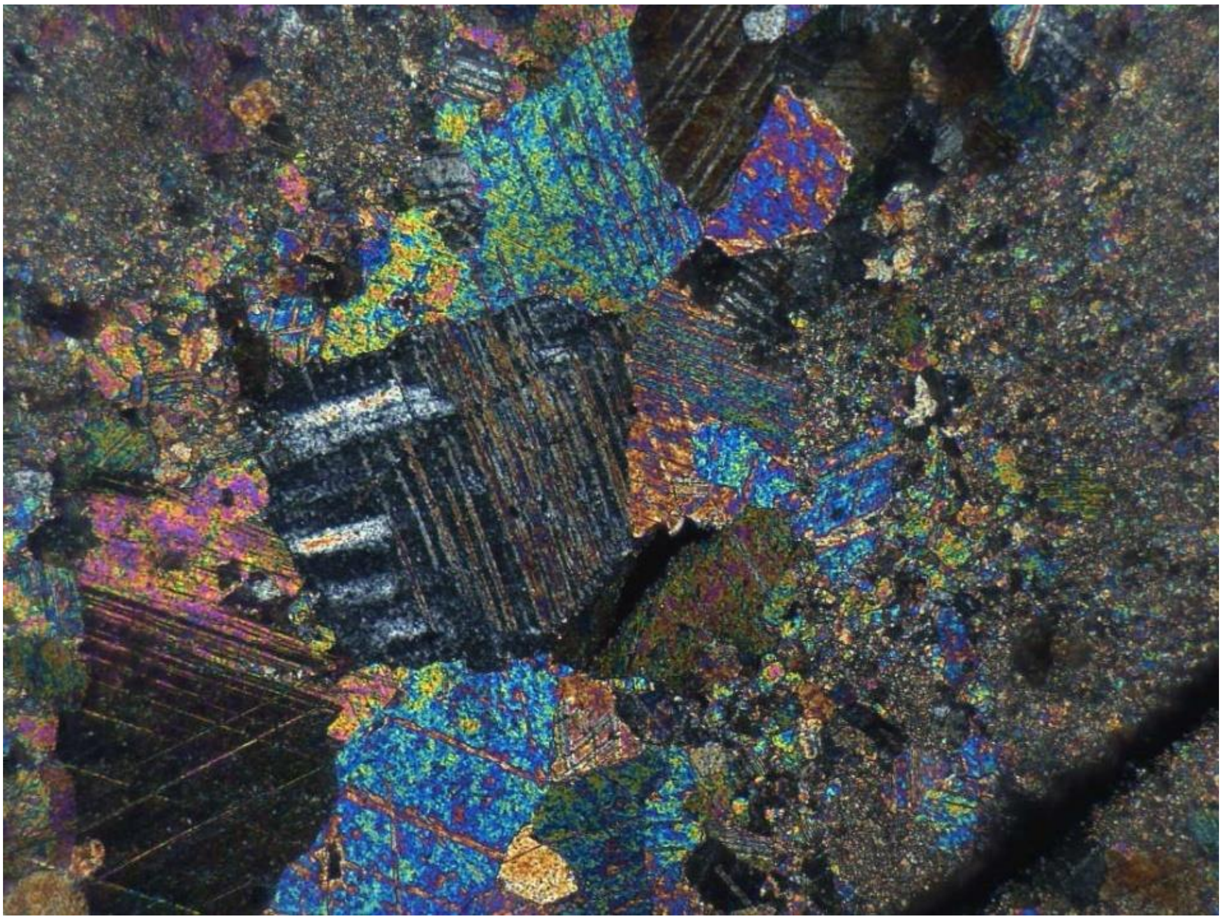


Plate No. 11- Calcite grains showing perfect 3 set of cleavage

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CHAPTER V

GEOCHEMISTRY

5.1 Introduction

Geochemistry can be broadly defined as the science concerned with all geochemical studies involving chemical change. It includes the study of the distribution of elements in rocks and minerals along with the interaction between these earth elements. (Clarke, 1924).

The whole-rock geochemistry is a major interest to geologists as the process aids in identification of the various types of limestone deposits. The geochemistry of limestone is characterised by the concentration of LILE elements (Sr, Ba & P) and Rare Earth Elements. If they happen to be carbonatites of Igneous origin, they tend to have higher concentration of Sr, Ba and P with generally higher La/Lu ratios linked to the extent of their magmatic differentiation. While on the other hand, if they happen to be Sedimentary carbonate, they generally have lower concentration of Sr+Ba (<900ppm) and REE <30 (Fig.), unless badly contaminated by terrigenous particulate matter (Zhang et al. 2017). However, textural differences and geochemistry can be used for discriminating these rocks. Direct comparison of REE contents in carbonatite sedimentary limestone accidental ethics (Fig. ..) indicates that carbonatite is at least one order of magnitude richer in REE than Sedimentary limestones (eg. Rosatelli et al. 2010). Sr and Ba tend to be incorporated in aragonite that transformed in calcite, reducing its LILE content (Shiraishi et al. 2020).

Further, geochemistry helps for understanding the evolution and tectonic environment of the area. The present geochemical studies aim to decipher the genesis and the economic viability of the limestones from parts of Phek District, Nagaland.

5. 2 Major Element Geochemistry

Twenty (20) representative samples of limestone have been analyzed for their major, trace and rare earth element (REE) compositions. Studied limestone samples clearly represent a high calcite and low Mg characteristics. The major oxides composition, range and averages for the representative samples are presented in the Tables 1, 5 &6. The geochemical data (Major, Trace, REE and Loss on Ignition values) of limestone samples are given in Table1& 4. The samples show the content of SiO_2 varies from 0.31% to 9.45% with an average of 2.50%. Al_2O_3 ranges from 0.1% to 1.87% with an average of 0.48%.

The major element contents in limestone of the study area exhibit high CaO varying from 53.40% - 56.88%, with an average content of 55.43%. The Magnesium concentration ranges from 0.55% 1.84% with average content of 0.86%. The P_2O_5 concentration varies from 0.00% to 0.13% with an average of 0.04%. The concentration of Titanium Oxide ranges from 0.09% to 0.11% with an average concentration of 0.08%. The composition of Sodium oxide ranges from 0.03% to 0.05% with 0.03% as its average content. The content of Potassium Oxide ranges from 0.00% to 0.07% with 0.013% as its average content. The content of Ferrous Oxide ranges in between 0.02% to 0.51% with 0.12% as its average content. P_2O_5 content is regarded highly sensitive to the presence of micro-crypto apatite, which crystallizes over a wide range of range of conditions but in this case, it seems to be non- favourable as its content is almost negligible.

The presence of minerals like calcite (55.43%), magnesium (0.86%), and quartz (2.50%) are found considerable for the limestones studied in the Phek District of NOB. Chlorite and apatite are present in almost negligible amounts.

5.3 Loss on Ignition (LOI)

It is one such basic characteristic which enables us to know the concentrations of organic matters or unstable oxides such as $CaCO_3$. Here in the analysis done for LOI, it varies from 30% to 44%, with an average concentration of 36.7%. This variation is mostly due to the presence of unstable oxides of $CaCO_3$ as the presence of organic matters is very negligible in the samples studied.

S.No.	Sample	Sum	SiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	TiO2	P2O5	LOI
		(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
1	NOLW1/17	98.09	1.96	0.26	0.05	0.00	0.70	55.99	0.04	0.00	0.09	0.00	39.00
2	NOLW2/17	98.69	3.60	0.24	0.05	0.00	0.71	54.96	0.03	0.01	0.09	0.00	39.00
3	NOLZ2/17	98.42	1.68	0.92	0.10	0.00	0.78	55.76	0.04	0.01	0.09	0.06	39.00
4	NOLZ3/17	98.44	2.86	0.25	0.08	0.00	0.76	55.29	0.04	0.01	0.09	0.07	39.00
5	NOLZ4/17	98.52	3.83	0.89	0.03	0.00	0.73	54.90	0.03	0.01	0.09	0.00	38.00
6	NOLM1/17	98.11	3.59	0.83	0.04	0.00	0.69	55.84	0.03	0.00	0.09	0.00	37.00
7	NOLM2/17	97.90	3.96	1.87	0.51	0.01	1.81	56.60	0.03	0.00	0.11	0.01	33.00
8	NOLNT3/17	98.32	9.45	0.90	0.41	0.00	0.70	56.64	0.05	0.00	0.10	0.07	30.00
9	NOLNT4/17	97.57	2.73	0.17	0.07	0.00	0.61	55.81	0.04	0.00	0.09	0.05	38.00
10	NOLNL2/17	98.52	0.82	0.13	0.05	0.00	0.80	55.58	0.03	0.01	0.09	0.02	41.00
11	NOLNL8/17	98.22	0.31	0.08	0.02	0.01	0.70	54.97	0.03	0.00	0.09	0.02	42.00
12	NOLNL109/17	98.33	2.36	0.11	0.03	0.01	0.67	55.90	0.03	0.01	0.09	0.13	39.00
13	NOLL13/17	98.04	1.34	0.10	0.09	0.00	0.71	56.68	0.03	0.00	0.09	0.00	39.00
14	NOLP1/17	98.76	0.93	0.32	0.43	0.03	0.91	51.86	0.03	0.07	0.09	0.09	44.00
15	NOLP4/17	98.65	2.98	0.83	0.05	0.01	1.84	55.79	0.03	0.03	0.09	0.00	37.00
16	NOLP6/17	98.92	0.79	0.33	0.17	0.00	0.99	53.40	0.04	0.06	0.09	0.04	43.00
17	NOLS1/17	98.48	1.98	0.97	0.04	0.00	0.55	56.81	0.03	0.00	0.09	0.01	38.00
18	NOLS5/17	98.05	2.92	0.30	0.07	0.00	0.64	54.87	0.03	0.01	0.09	0.12	39.00
19	NOLS6/17	98.67	1.23	0.14	0.02	0.00	1.64	54.48	0.03	0.01	0.09	0.03	41.00
20	NOLS8/17	98.29	3.07	0.40	0.11	0.00	0.58	56.88	0.04	0.04	0.09	0.08	37.00
21	JLs-1*	99.55	0.10	0.02	0.01	0.00	0.61	55.01	0.00	0.00	0.00	0.06	43.73

Table No. 03: Major oxide weight (%) composition of limestones

Oxides	Representative Limestone Samples		
	Min.	Max.	Average
SiO_2	0. 31	9.45	2.50
TiO_2	0.09	0.11	0.08
Al_2O_3	0.10	1.87	0.48
Fe_2O_3	0.02	0.51	0.12
MnO	0.06	0.25	0.15
MgO	0.55	1.84	0.86
CaO	53.40	56.88	55.43
Na_2O	0.03	0.05	0.032
K_2O	0.00	0.07	0.013
P_2O_5	0.00	0.13	0.04

Table No. 04: Range and averages of major oxides of the Representative Rock Samples of Limestones

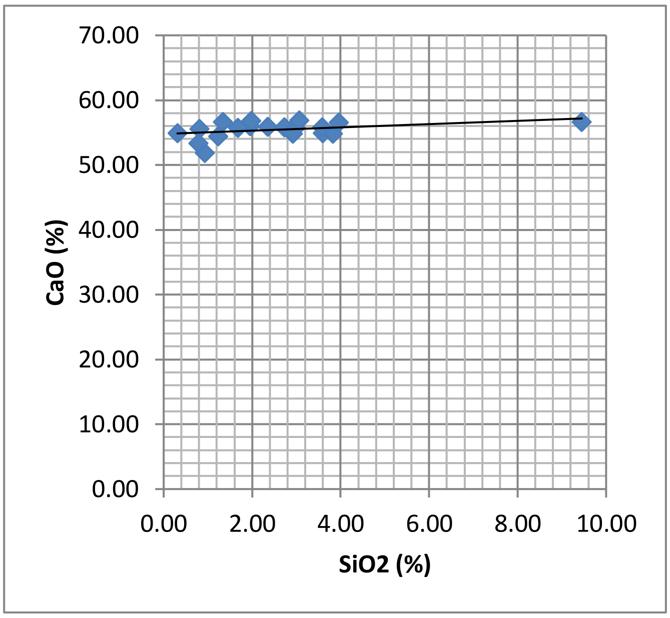


Fig. No. 04: CaO vs. SiO_2 plot

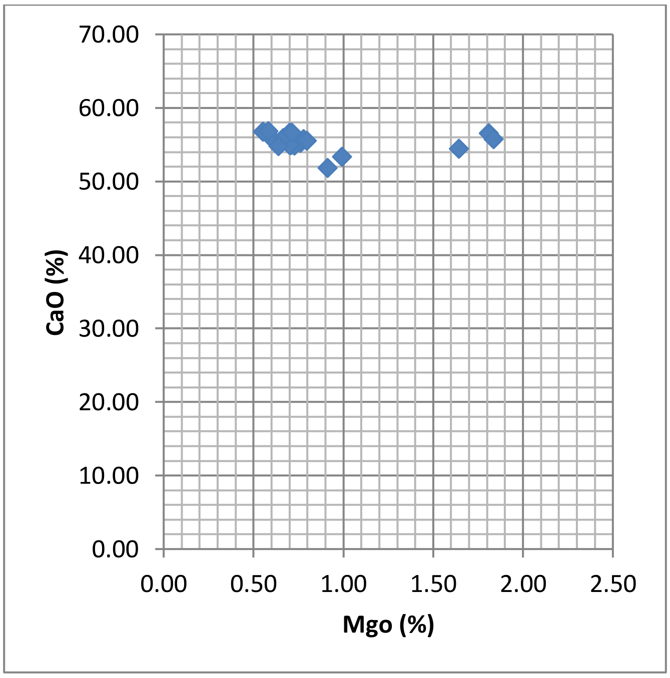
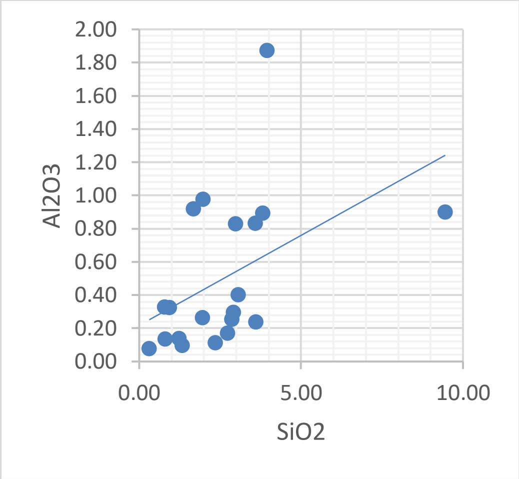
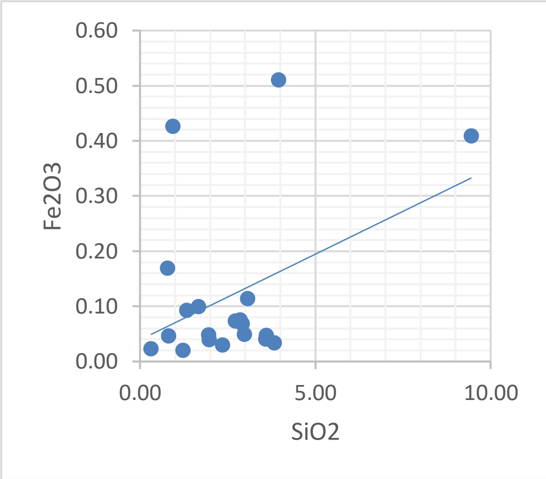
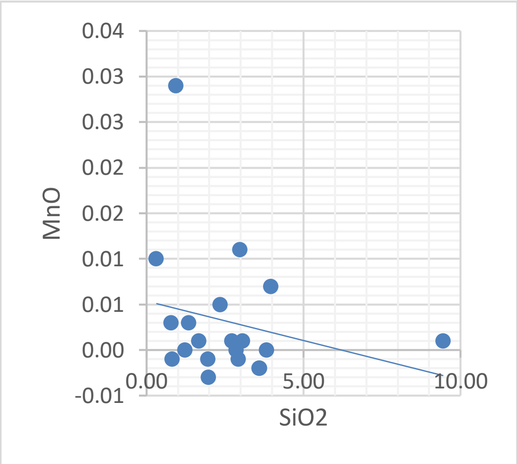


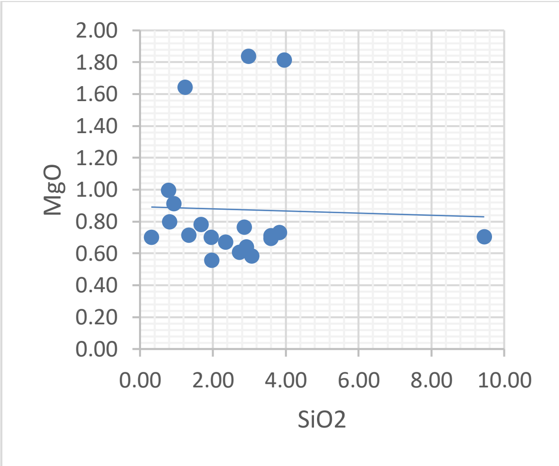
Fig. No. 05: Cao vs. MgO plot


Al2O3
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0.00
5.00
10.00
SiO2

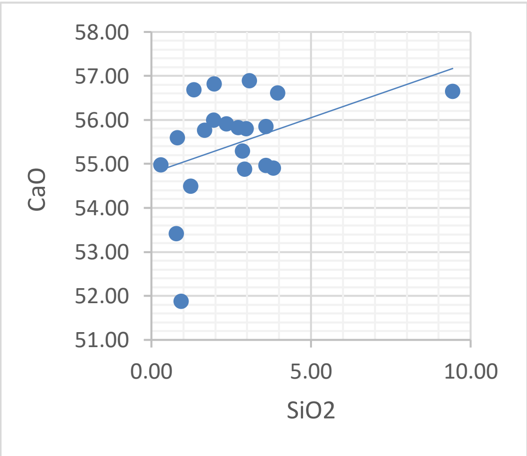

Fe2O3
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0.00
5.00
10.00
SiO2

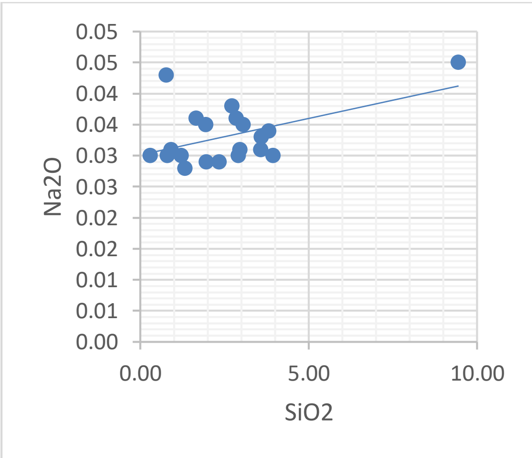
a **b**


MnO
0.04
0.03
0.03
0.02
0.02
0.01
0.01
0.00
-0.01
0.00
5.00
10.00
SiO2

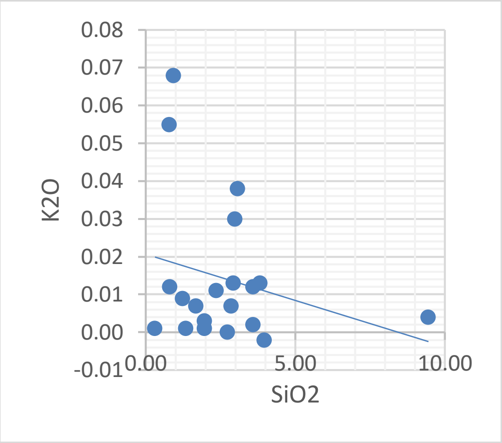

MgO
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0.00
2.00
4.00
6.00
8.00
10.00
SiO2

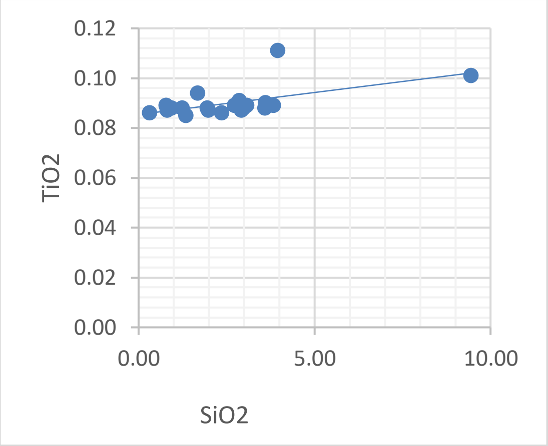
c **d**


CaO
58.00
57.00
56.00
55.00
54.00
53.00
52.00
51.00
0.00
5.00
10.00
SiO2


Na2O
0.05
0.05
0.04
0.04
0.03
0.03
0.02
0.02
0.01
0.01
0.00
0.00
5.00
10.00
SiO2

e **f**





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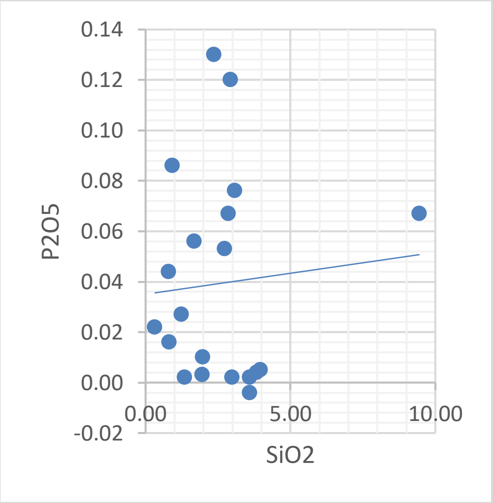
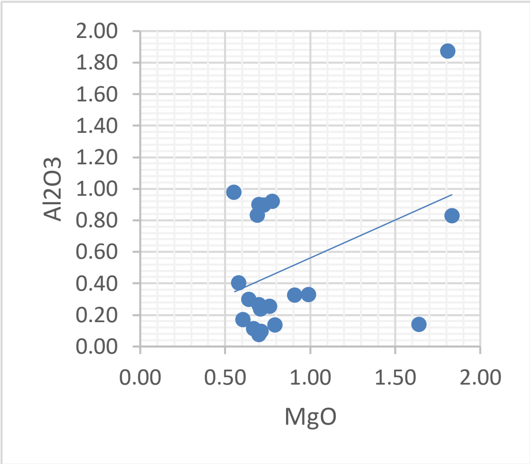
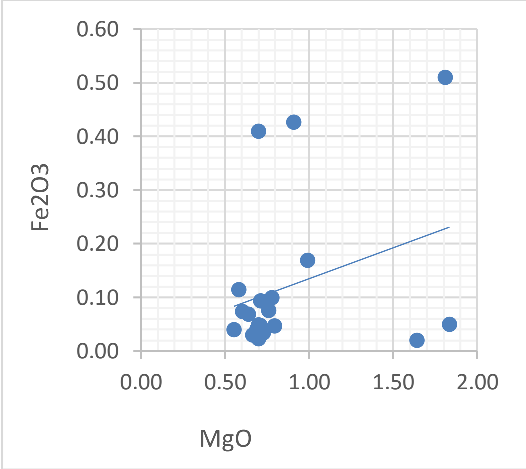


i

Fig. No. 06: Bivariate variation diagrams of SiO_2 against Major Oxides (after Harker, 1909)



a



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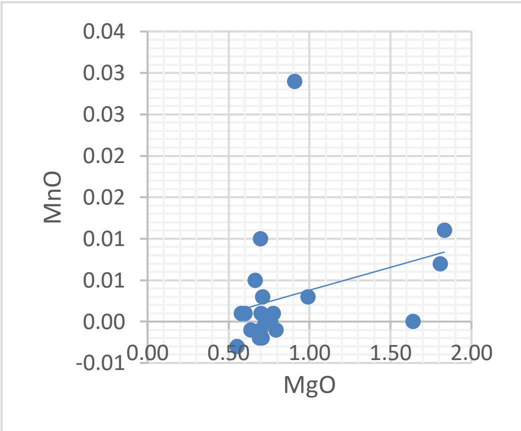
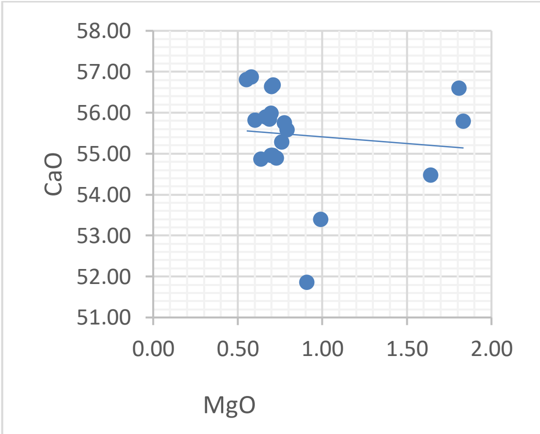


c



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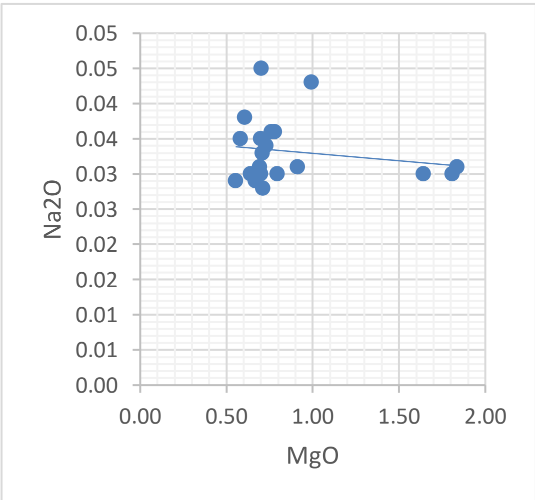

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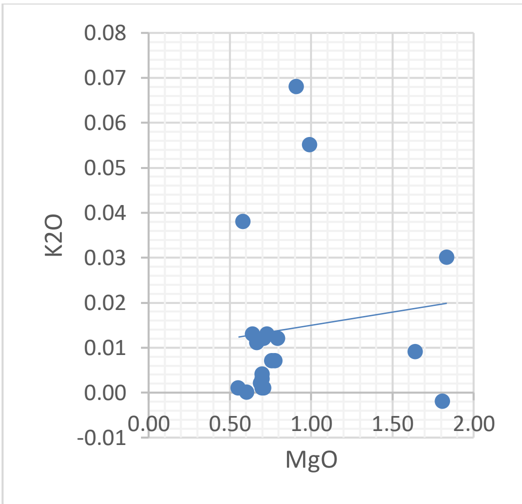

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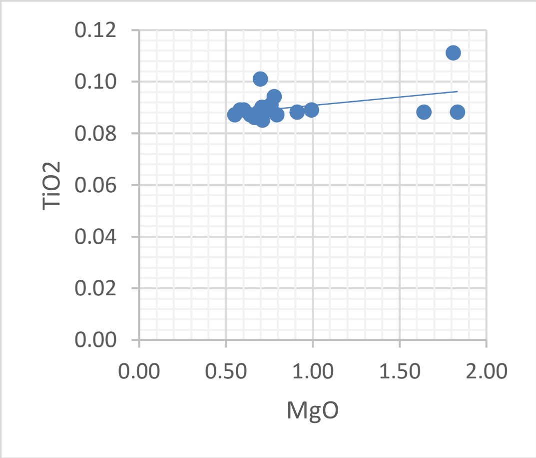

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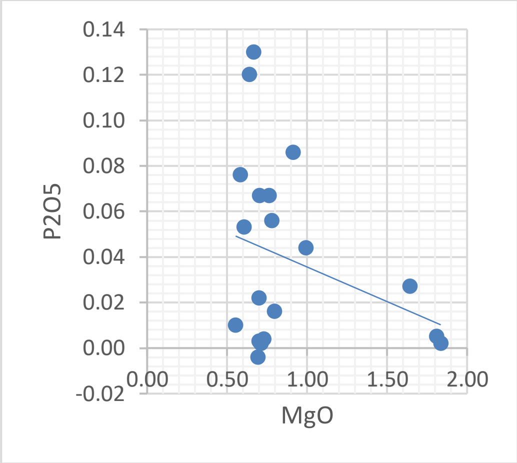


h

Fig. No. 07: Bivariate variation diagrams of MgO against Major Oxides (after Harker, 1909)

5.4 Behaviour of Major Elements

- **SiO_2 with other major oxides**

P_2O_5 and Na_2O decreases regularly with decrease of SiO_2 which shows a Para -sympathetic relationship, whereas MgO and CaO relationship with SiO_2 are almost linear relations. SiO_2relationship with MnO and K_2O is weakly antipathetic and with TiO_2, $Al_2O_3$and Fe_2O_3, does not show any significant relationship exhibiting almost horizontal distribution. These relationships are shown in Harker linear variation diagram (Fig. No. 06).

- **MgO with other major oxides**

Strong sympathetic relationship was observed between MgO versus with the major oxides Al_2O_3, Na_2O and P_2O_5 whereas CaO vs. MgO shows sympathetic relationship**.** K_2O, MnO, Fe_2O_3 and TiO_2 relationship with respect to MgO are weakly antipathetic as they are horizontally distributed against each other. The overall observation indicates that MgO decreases with an increase of all major oxides except CaO. (Fig. No. 07)

5.5 Trace Elements Geochemistry

Trace element distribution becomes a reliable guide and indicators of chemical processes for the evolution of carbonate systems, which further helps in understanding the original nature of the rocks even when they are intensely metamorphosed, as it is also considered. In the recent studies on trace elements, variations in rocks have been stressed. The trace elements that are among the most abundant in the earth crust or may be rare earth elements that have a low abundance in the earth crust as a whole. Both igneous and their metamorphosed equivalents have a wide range trace element concentration and as such no completely diagnostic abundance criteria have been discovered. However, high content Sr in limestones have received much comment.

The behaviour of trace elements during fractional crystallisation of basic magma of Skergaard intrusion, East Greenland was investigated by Wager and Mitchell (1951). The distribution of the elements in various types of rocks was earlier given by Turekian and Wedepohl (1961). They suggested that the metamorphic rocks generally retain a chemical composition similar to their un-metamorphosed equivalents. The principle governing the entry of trace elements into a mineral was formulated by Pauling (1960) and Goldschmidt (1937 & 1954), which depends on its availability, chemical nature, ionic charge and ionic radius. In recent years three principles of camouflage, capture and admission are known as Goldsmith's rule. Properties such as electro negativity, polarisability, absorption and coordination number may also influence the distribution of elements in addition to the ionic charge and radius elements (Fyfe, 1954; Ramberg, 1952; Ahrene, 1964; Rao, 1985).

Trace element concentrations (ppm), their range and averages of limestones from the study area are given in Table No. 2. Sc ranges between 0.12-0.24 with an average of 0.30**;** V ranges between 1.55-20.45, obtaining an average of 11.10; Cr is ranged between 4.55-30.80, with 16.40 as its average value; Co ranges between 0.11-0.51; Ni ranges between 2.7-6.54; Cu ranges from 1.05-4.95; Zn rages from 28.57-66.14; Ga ranges between 0.06-0.36; Rb ranges between 1.57-5.57; Sr ranges between 117.51-952.52; Y ranges between 0.66-11.25; Zr ranges between 4.89-16.62; Nb ranges from 0.35-.51; Cs ranges between 0.01-0.06; Ba ranges between 2.26-24.48; Hf ranges between 0.07-0.26; Ta ranges between 0.01-0.34; Pb ranges from 0.57-

1.71; Th ranges from 0.03-0.11; and the last of the trace element U ranges between 0.25-2.70. The average concentration of Trace elements (ppm) varies from 0.1 to 561.30. Trace elements like Sc, Co, Ga, Cs, Ba, Hf, Ta and Th show negligible presence falling lesser than 1ppm; and trace elements like V, Cr, Ni, Cu, Rb, Y, Zr, Nb, Ba, Pb and U fall within a considerable range between 1-20 ppm. But the high concentration of Sr is of great interest to be considered carefully.

CV- Certified Value; OV- Obtained Value													
All values are in ug/g or ppm													
Analyte	**JDO1 (CV)**	**JDO1 (OV)**	**Z3-17**	**W1-17**	**SS1-17**	**L2-17**	**W2-17**	**Z2-17**	**L13-17**	**L101-17**	**L8-17**	**JLS-1**	**JDO1 (OV)**
Sc(45)	0.14	0.14	0.18	0.15	0.15	0.14	0.12	0.17	0.17	0.13	0.14	0.15	0.16
V(51)	3.14	3.09	1.55	1.55	2.91	12.30	1.62	1.74	3.05	2.67	2.85	4.51	3.12
Cr(53)	7.00	6.87	5.65	5.75	4.96	8.81	4.54	5.24	6.55	5.52	5.07	6.49	6.86
Co(59)	0.17	0.16	0.33	0.18	0.16	0.17	0.16	0.27	0.16	0.21	0.17	0.51	0.19
Ni(60)	2.90	2.79	3.94	2.65	2.53	2.37	2.40	2.97	2.39	2.56	2.30	3.11	2.40
Cu(63)	1.40	1.35	1.45	1.38	1.79	1.28	1.05	1.56	1.12	1.41	1.05	3.10	1.40
Zn(66)	34.40	33.41	38.15	34.58	34.29	37.95	33.12	44.69	31.84	51.41	28.57	52.01	33.99
Ga(71)	0.10	0.10	0.10	0.09	0.10	0.08	0.07	0.12	0.06	0.09	0.06	0.13	0.09
Rb(85)	2.00	1.71	2.18	2.12	1.97	1.95	1.84	2.25	1.72	2.35	1.57	4.11	1.90
Sr(88)	119.00	113.78	133.25	209.64	257.95	230.20	183.71	117.51	265.93	259.24	210.80	293.76	119.33
Y(89)	11.20	10.73	1.38	0.82	2.75	1.90	0.67	1.45	0.74	2.37	1.08	1.36	11.21
Zr(90)	6.21	5.99	6.62	5.61	4.90	5.45	7.52	8.95	8.24	7.55	5.34	5.01	6.34
Nb(93)	0.60	0.61	0.81	0.61	0.55	0.57	0.59	0.85	0.41	0.53	0.35	0.58	0.55
Cs(133)	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.05	0.02
Ba(137)	6.14	5.82	3.41	24.48	7.87	2.88	2.46	5.56	4.12	9.18	2.26	50.60	6.24
La(139)	7.93	7.56	1.48	1.10	2.57	1.64	0.85	1.73	0.97	3.37	1.46	2.31	8.00
Ce(140)	2.54	2.43	1.70	1.79	1.90	1.85	1.30	2.13	1.00	2.68	1.16	3.62	2.64
Pr(141)	0.96	0.94	0.25	0.21	0.41	0.30	0.16	0.30	0.15	0.48	0.21	0.45	0.95
Nd(146)	5.33	5.26	1.15	0.90	1.91	1.36	0.69	1.35	0.61	2.11	0.87	2.27	5.29
Sm(147)	0.84	0.79	0.24	0.18	0.41	0.29	0.14	0.28	0.12	0.44	0.17	0.39	0.82
Eu(153)	0.19	0.19	0.05	0.06	0.10	0.08	0.03	0.06	0.03	0.09	0.05	0.10	0.18

Batch 1 contd.													
Gd(157)	1.80	1.83	0.20	0.14	0.37	0.26	0.11	0.23	0.11	0.36	0.15	0.60	1.82
Tb(159)	0.12	0.12	0.03	0.02	0.06	0.05	0.02	0.04	0.02	0.06	0.03	0.04	0.11
Dy(163)	1.00	0.99	0.21	0.13	0.42	0.30	0.11	0.23	0.12	0.38	0.17	0.27	0.96
Ho(165)	0.67	0.64	0.05	0.03	0.10	0.07	0.02	0.05	0.03	0.09	0.04	0.15	0.64
Er(166)	0.44	0.43	0.16	0.09	0.32	0.20	0.07	0.16	0.08	0.26	0.11	0.09	0.42
Tm(169)	0.06	0.06	0.02	0.01	0.04	0.03	0.01	0.02	0.01	0.03	0.01	0.01	0.06
Yb(172)	0.36	0.36	0.17	0.09	0.28	0.17	0.07	0.17	0.07	0.20	0.09	0.09	0.35
Lu(175)	0.05	0.05	0.03	0.02	0.04	0.03	0.01	0.03	0.01	0.03	0.01	0.01	0.05
Hf(178)	0.10	0.09	0.10	0.09	0.08	0.09	0.12	0.13	0.12	0.12	0.08	0.07	0.09
Ta(181)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Pb(208)	1.00	0.97	1.05	1.58	1.26	0.69	0.84	1.40	0.74	1.71	0.78	1.18	0.98
Th(232)	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.07	0.03	0.06	0.04	0.06	0.05
U(238)	0.86	0.84	0.27	0.29	0.81	2.52	0.49	0.30	0.47	0.79	0.64	1.64	0.82

Table No. 05: Trace and REE analysis data of limestones from parts of Phek District, Nagaland (Batch 1)

Analyte	JDO-1 (CV)	JDO-1 (OV)	P1-17	NT4-17	P4-17	M2-17	Z4-17	NT3-17	P6-17	S8-17	M1-17	S6-17	S1-17	L2-17 (D)	JDO-1 (OV)
Sc(45)	0.14	0.15	0.24	0.16	0.20	0.23	0.17	0.18	0.19	0.24	0.21	0.13	0.18	0.15	0.14
V(51)	3.14	4.19	14.21	1.93	3.65	7.75	4.11	5.44	9.64	7.78	5.23	20.45	4.99	16.26	3.66
Cr(53)	7.00	9.15	8.80	6.49	6.52	30.80	7.03	8.13	15.36	7.18	10.90	8.26	7.19	10.78	8.06
Co(59)	0.17	0.12	0.36	0.13	0.29	0.51	0.34	0.33	0.35	0.40	0.51	0.34	0.38	0.28	0.14
Ni(60)	2.90	4.58	6.54	4.40	5.00	5.81	5.31	5.20	4.88	4.95	6.31	4.34	4.10	4.09	3.73
Cu(63)	1.40	1.79	3.75	1.56	3.54	3.60	3.57	3.51	3.36	3.83	4.95	3.44	3.39	3.25	1.59
Zn(66)	34.40	40.26	42.52	35.77	47.52	30.38	40.66	40.61	46.13	44.34	66.14	37.02	29.72	56.52	37.25
Ga(71)	0.10	0.11	0.24	0.09	0.16	0.36	0.15	0.18	0.24	0.21	0.21	0.16	0.16	0.13	0.11
Rb(85)	2.00	1.95	5.10	1.97	3.77	3.43	3.82	3.50	3.99	4.26	5.57	3.65	4.71	3.26	1.97
Sr(88)	119.00	121.06	324.11	202.66	283.58	952.52	144.78	191.04	299.41	173.94	219.23	792.79	306.59	247.63	119.65
Y(89)	11.20	11.31	4.31	1.89	4.51	3.14	1.17	2.90	4.91	4.98	1.56	1.17	2.02	2.38	11.25
Zr(90)	6.21	6.04	16.62	7.54	6.38	14.85	8.82	4.90	9.11	6.34	12.75	5.54	5.78	6.91	6.11
Nb(93)	0.60	0.56	0.89	1.18	0.61	3.51	0.73	1.75	1.16	0.76	0.78	0.64	0.56	0.72	0.58
Cs(133)	0.02	0.02	0.05	0.02	0.04	0.04	0.04	0.04	0.04	0.05	0.06	0.04	0.05	0.03	0.02
Ba(137)	6.14	5.23	3.48	2.87	5.08	4.12	3.05	12.81	3.04	4.96	3.82	3.80	3.12	4.87	5.66
La(139)	7.93	7.53	7.72	2.10	4.19	3.75	1.94	3.01	7.27	5.51	2.62	1.71	2.74	2.75	7.72
Ce(140)	2.54	2.41	4.87	1.86	3.36	5.28	2.79	3.38	5.43	3.43	3.84	2.61	3.57	3.31	2.47
Pr(141)	0.96	0.90	1.08	0.33	0.70	0.78	0.38	0.55	1.11	0.84	0.50	0.35	0.53	0.51	0.93
Nd(146)	5.33	5.07	5.79	1.78	3.92	4.20	1.89	2.97	5.91	4.71	2.57	1.81	2.84	2.48	5.20
Sm(147)	0.84	0.81	0.85	0.32	0.72	0.72	0.32	0.52	0.97	0.84	0.43	0.31	0.51	0.46	0.82
Eu(153)	0.19	0.18	0.20	0.07	0.17	0.20	0.06	0.13	0.23	0.19	0.09	0.06	0.14	0.10	0.19

Batch-2 Contd.															
Gd(157)	1.80	1.74	0.69	0.27	0.63	0.58	0.23	0.44	0.79	0.70	0.31	0.23	0.41	0.38	1.77
Tb(159)	0.12	0.11	0.11	0.04	0.11	0.09	0.03	0.07	0.13	0.12	0.04	0.03	0.06	0.06	0.11
Dy(163)	1.00	0.96	0.71	0.30	0.73	0.53	0.20	0.47	0.81	0.80	0.26	0.20	0.36	0.39	0.98
Ho(165)	0.67	0.64	0.15	0.07	0.16	0.11	0.04	0.10	0.17	0.18	0.05	0.04	0.07	0.09	0.65
Er(166)	0.44	0.43	0.44	0.21	0.47	0.29	0.12	0.30	0.49	0.53	0.16	0.11	0.16	0.24	0.43
Tm(169)	0.06	0.06	0.06	0.03	0.07	0.04	0.02	0.04	0.07	0.07	0.02	0.02	0.02	0.03	0.06
Yb(172)	0.36	0.35	0.38	0.19	0.40	0.25	0.11	0.28	0.41	0.53	0.13	0.10	0.13	0.21	0.35
Lu(175)	0.05	0.05	0.06	0.03	0.06	0.04	0.02	0.04	0.06	0.08	0.02	0.01	0.01	0.03	0.05
Hf(178)	0.10	0.09	0.26	0.11	0.10	0.23	0.13	0.08	0.14	0.10	0.19	0.08	0.09	0.11	0.10
Ta(181)	0.01	0.01	0.02	0.34	0.01	0.13	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.01
Pb(208)	1.00	0.94	0.97	0.88	0.75	0.57	0.83	1.02	0.73	0.90	1.14	0.76	0.62	1.14	0.97
Th(232)	0.04	0.04	0.11	0.03	0.05	0.07	0.06	0.05	0.15	0.05	0.06	0.04	0.04	0.10	0.04
U(238)	0.86	0.83	0.94	0.38	0.29	0.26	0.40	0.66	0.49	1.01	0.39	1.90	0.48	2.70	0.84

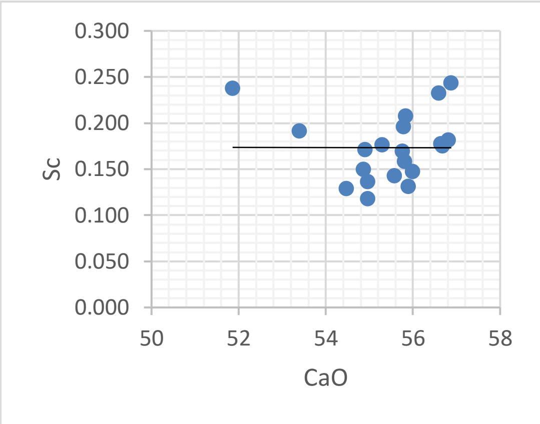
Table No. 06: Trace and REE analysis data of limestones from parts of Phek District, Nagaland (Batch 2)

Sl. No.	Trace element	Average
1	Sc	0.03
2	V	11.10
3	Cr	16.40
4	Co	0.56
5	Ni	8.10
6	Cu	4.80
7	Zn	79.10
8	Rb	6.00
9	Sr	561. 30
10	Y	4.40
11	Zr	16.40
12	Nb	1.90
13	Cs	0.10
14	Ba	11.50
15	Hf	0.20
16	Ta	0.10
17	Pb	1.90
18	Th	0.10
19	U	1.40

Table No. 07: Average of Trace elements

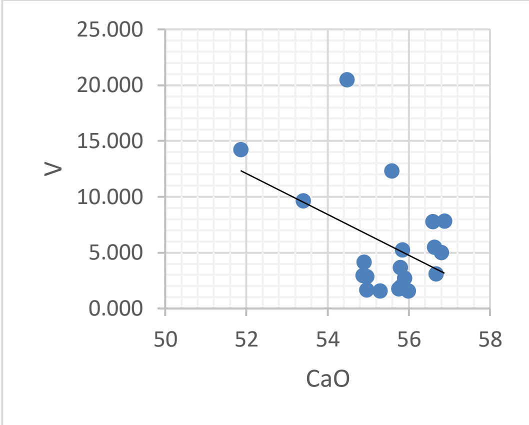
Sl. no	Trace element	Representative Limestone Samples	Mid-Atlantic ridge
1	Sc	0.30	00
2	V	11.10	40
3	Cr	16.40	2400
4	Co	0.60	110
5	Ni	8.10	-1500
6	Cu	4.80	-20
7	Zn	79.10	00
8	Rb	6.00	-1
9	Sr	561. 30	-20
10	Y	4.40	00
11	Zr	16.40	30.45
12	Hf	0.20	00
13	Nb	1.90	00
14	Ta	0.10	00
15	Cs	0.10	00
16	Ba	11.50	-0.4
17	Pb	1.90	0.05
18	Th	0.10	-0.06
19	U	1.40	-0.02

Table No. 08: Comparison of Trace elements of Representative Limestone samples with Mid-Atlantic ridge



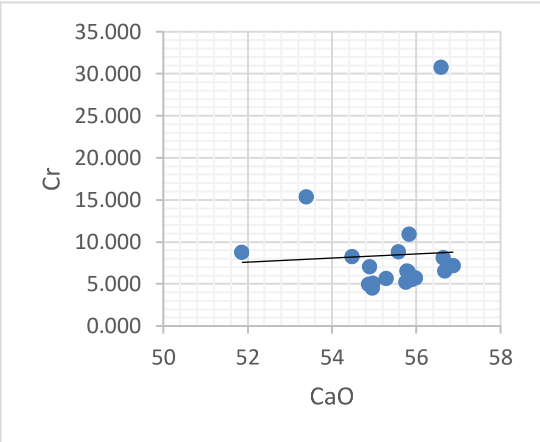
Sc
0.300
0.250
0.200
0.150
0.100
0.050
0.000
50
52
54
56
58
CaO

a



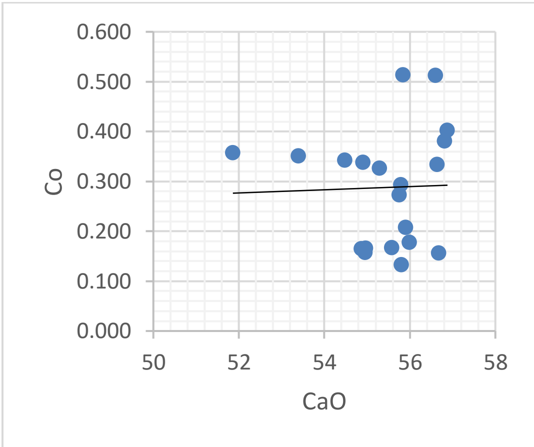
V
25.000
20.000
15.000
10.000
5.000
0.000
50
52
54
56
58
CaO

b



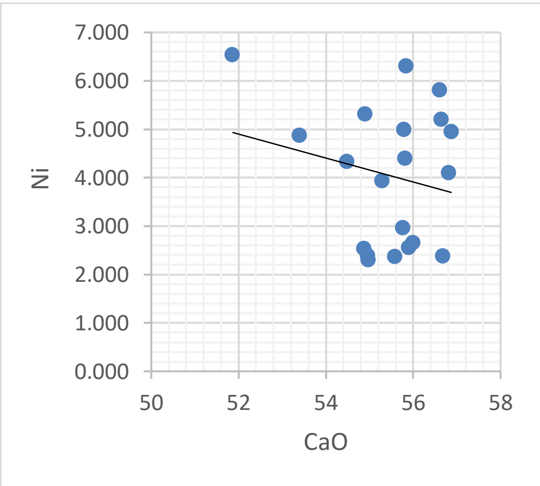
Cr
35.000
30.000
25.000
20.000
15.000
10.000
5.000
0.000
50
52
54
56
58
CaO

c



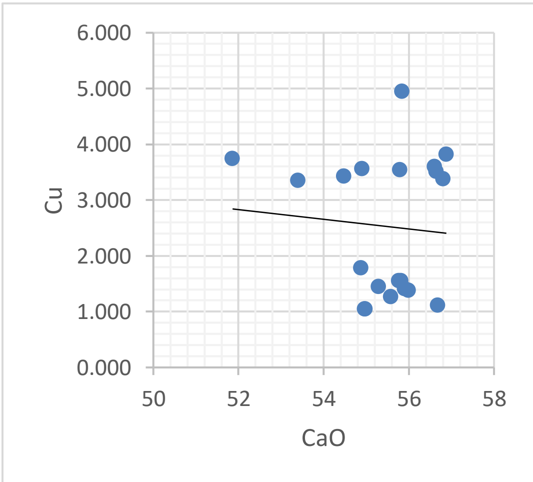
Co
0.600
0.500
0.400
0.300
0.200
0.100
0.000
50
52
54
56
58
CaO

d



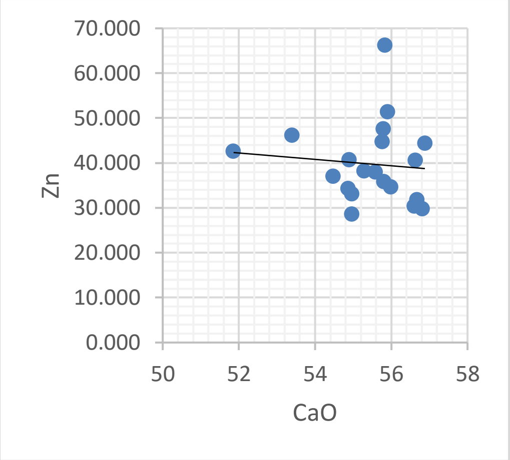
Ni
7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
50
52
54
56
58
CaO

e

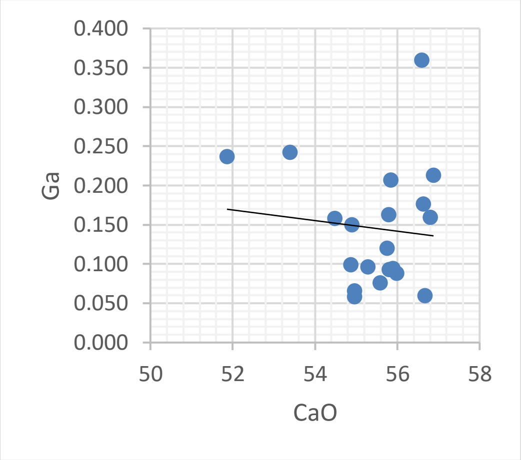


Cu
6.000
5.000
4.000
3.000
2.000
1.000
0.000
50
52
54
56
58
CaO

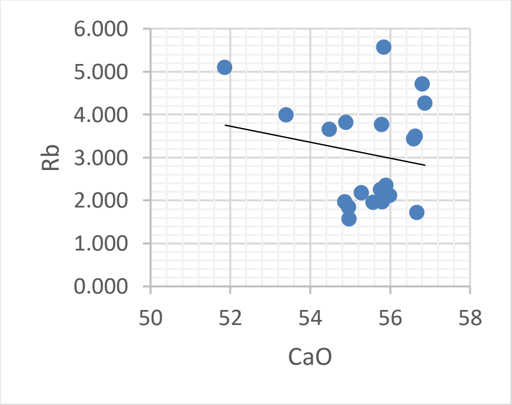
f


70.000
60.000
50.000
40.000
30.000
20.000
10.000
0.000
Zn
50
52
54
56
58
CaO

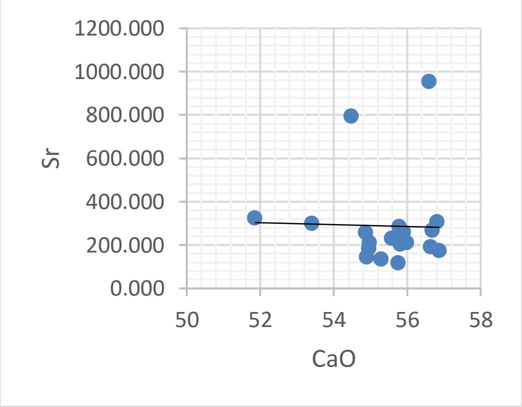
g


0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000
Ga
50
52
54
56
58
CaO

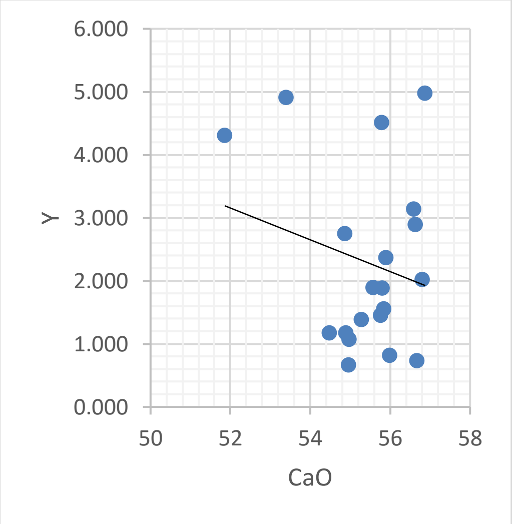
h


6.000
5.000
4.000
3.000
2.000
1.000
0.000
Rb
50
52
54
56
58
CaO

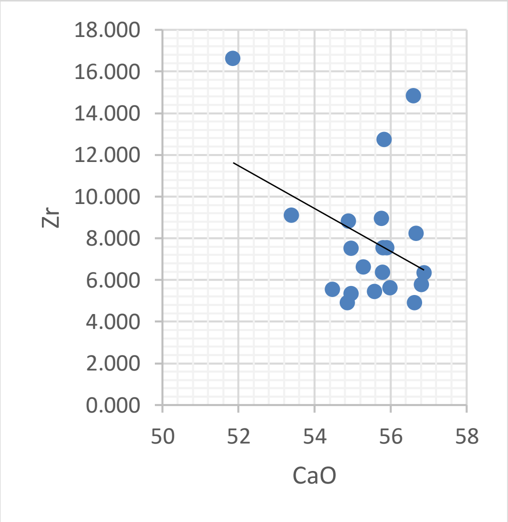
i


1200.000
1000.000
800.000
600.000
400.000
200.000
0.000
Sr
50
52
54
56
58
CaO

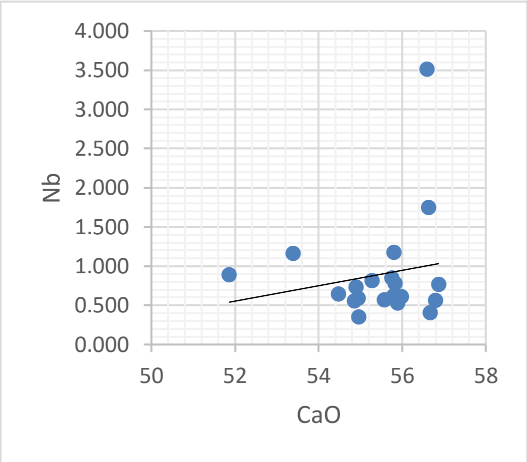
j


6.000
5.000
4.000
3.000
2.000
1.000
0.000
Y
50
52
54
56
58
CaO

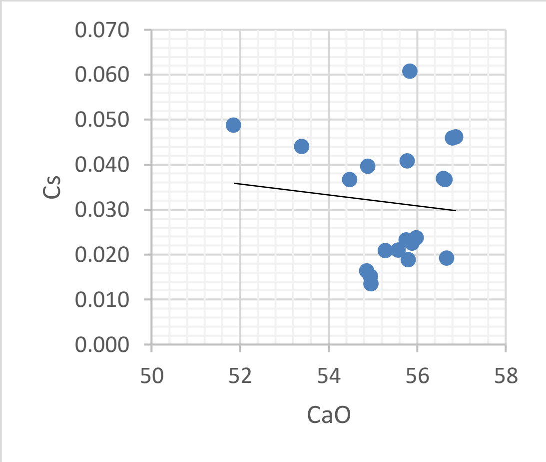
k


18.000
16.000
14.000
12.000
10.000
8.000
6.000
4.000
2.000
0.000
Zr
50
52
54
56
58
CaO

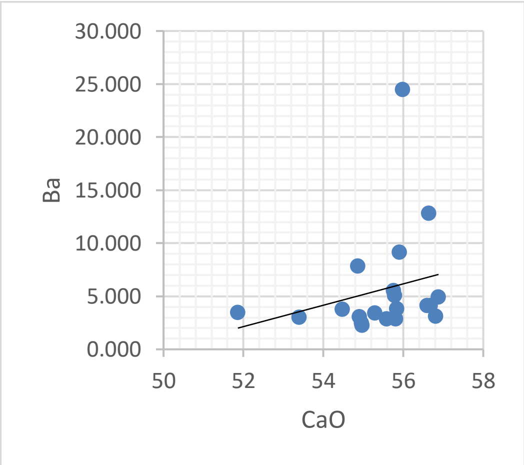
l


Nb
CaO
4.000
3.500
3.000
2.500
2.000
1.500
1.000
0.500
0.000
50
52
54
56
58

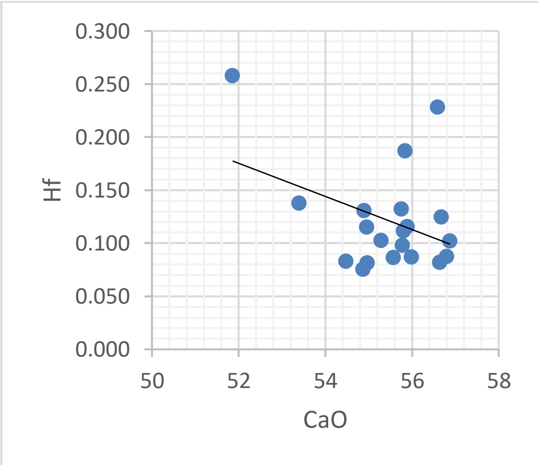
m


Cs
CaO
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
50
52
54
56
58

n


Ba
CaO
30.000
25.000
20.000
15.000
10.000
5.000
0.000
50
52
54
56
58

o


Hf
CaO
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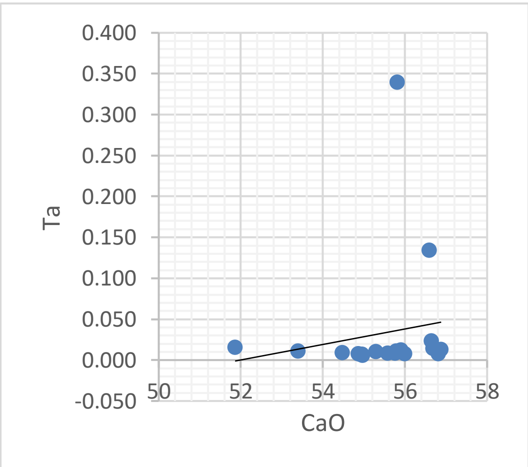
0.250
0.200
0.150
0.100
0.050
0.000
50
52
54
56
58

p


Ta
CaO
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0.300
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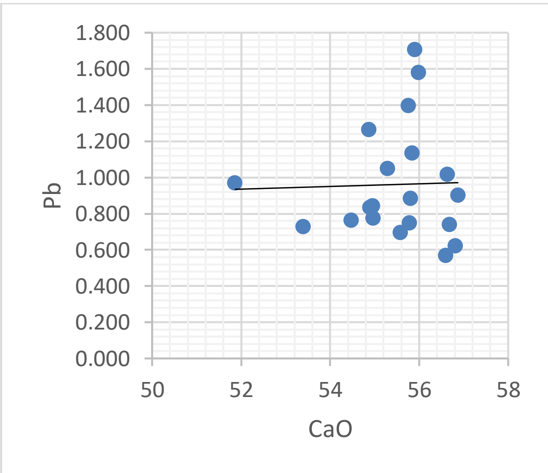
0.150
0.100
0.050
0.000
-0.050
50
52
54
56
58

q


Pb
CaO
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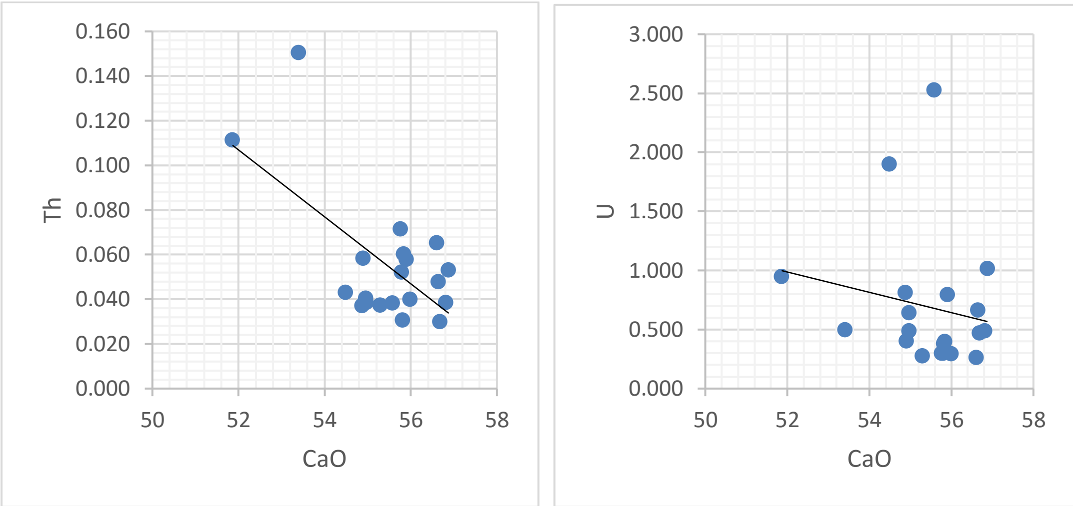
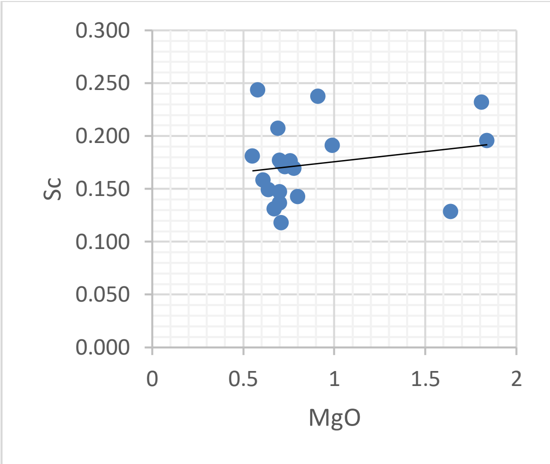
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
50
52
54
56
58

r

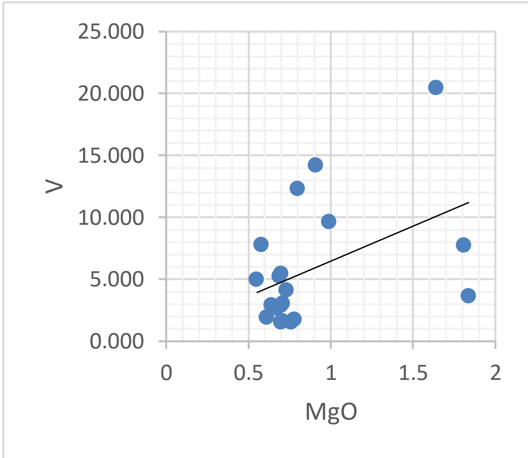


s **t**

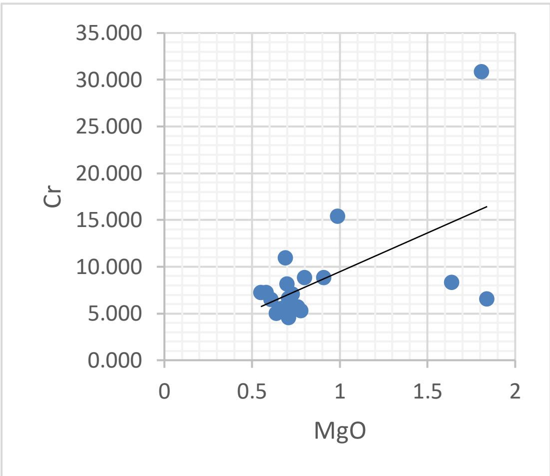
Fig. No. 08: Bivariate variation diagrams of CaO against Trace elements (after Harker, 1909)


Sc
0.300
0.250
0.200
0.150
0.100
0.050
0.000
0
0.5
1
1.5
2
MgO

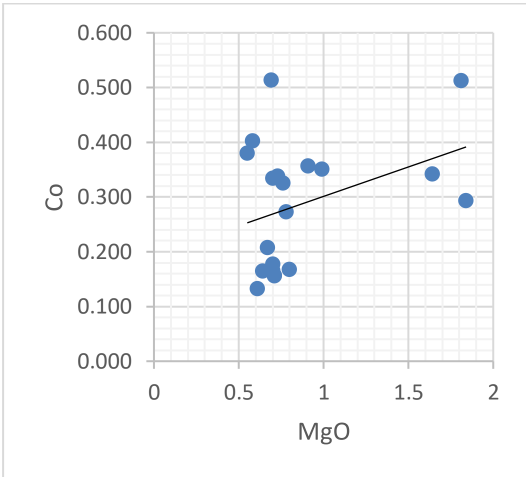
a


V
25.000
20.000
15.000
10.000
5.000
0.000
0
0.5
1
1.5
2
MgO

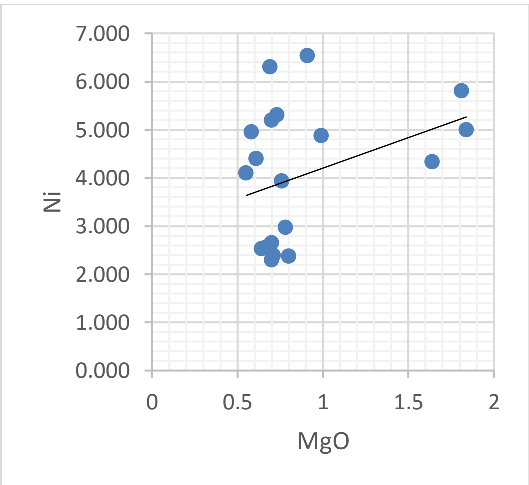
b


Cr
35.000
30.000
25.000
20.000
15.000
10.000
5.000
0.000
0
0.5
1
1.5
2
MgO

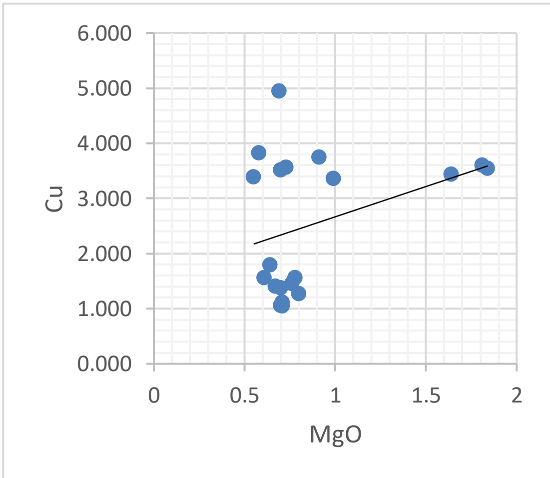
c


Co
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0
0.5
1
1.5
2
MgO

d


Ni
7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
0
0.5
1
1.5
2
MgO

e


Cu
6.000
5.000
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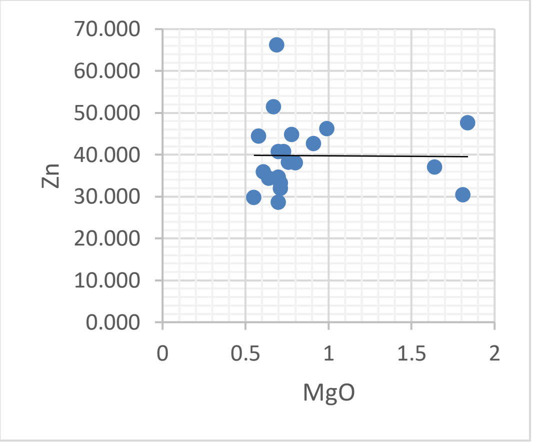
3.000
2.000
1.000
0.000
0
0.5
1
1.5
2
MgO

f


Zn
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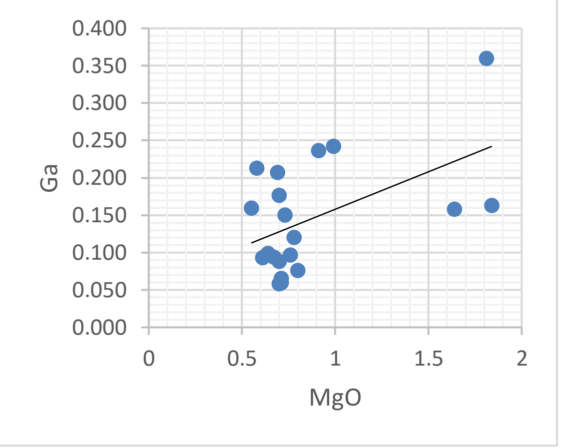
60.000
50.000
40.000
30.000
20.000
10.000
0.000
0
0.5
1
1.5
2
MgO


Ga
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0.300
0.250
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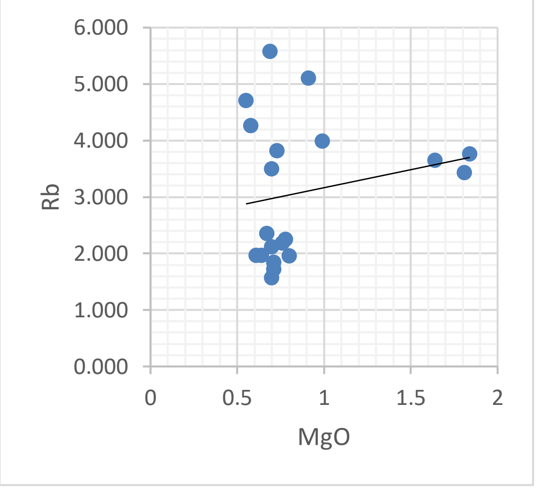
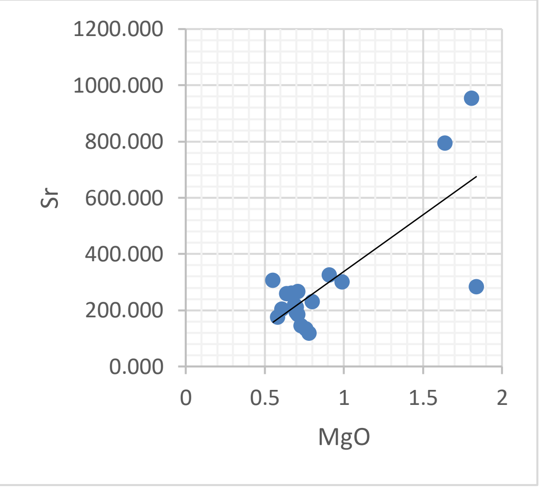
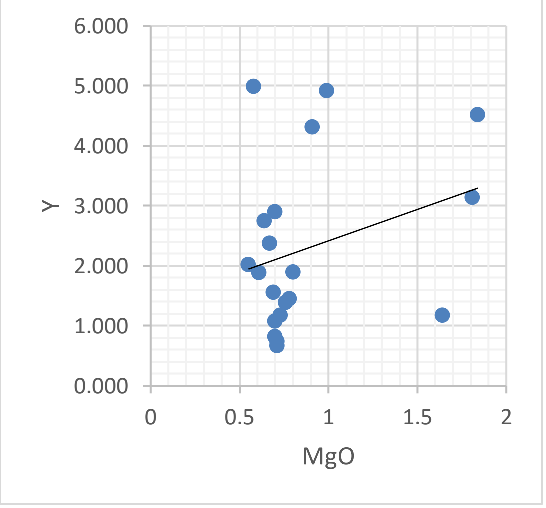
0.150
0.100
0.050
0.000
0
0.5
1
1.5
2
MgO

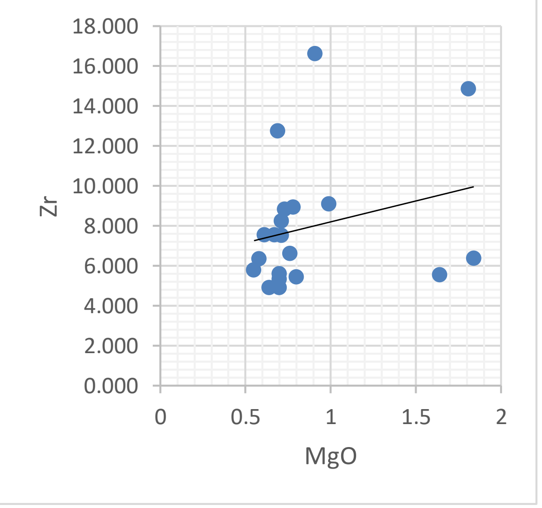
g **h**


Rb
6.000
5.000
4.000
3.000
2.000
1.000
0.000
0
0.5
1
1.5
2
MgO

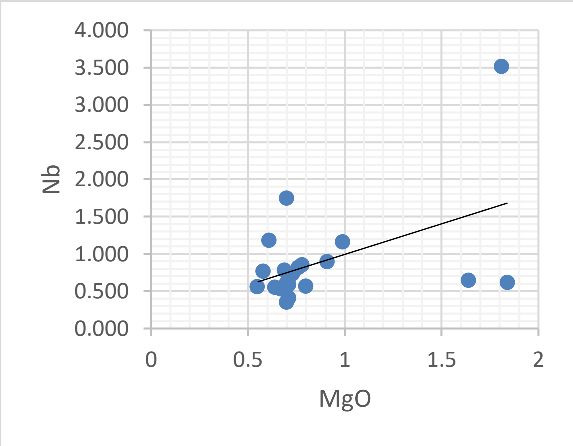

Sr
1200.000
1000.000
800.000
600.000
400.000
200.000
0.000
0
0.5
1
1.5
2
MgO

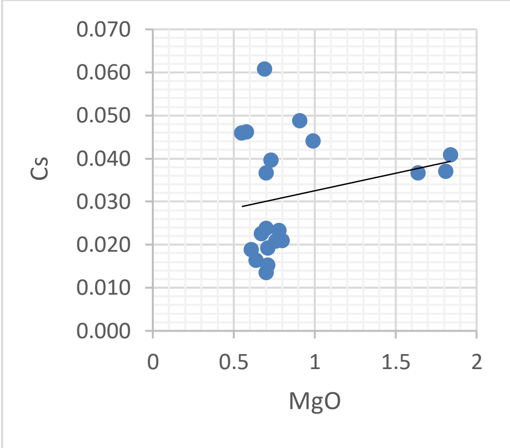
i **j**


Y
6.000
5.000
4.000
3.000
2.000
1.000
0.000
0
0.5
1
1.5
2
MgO

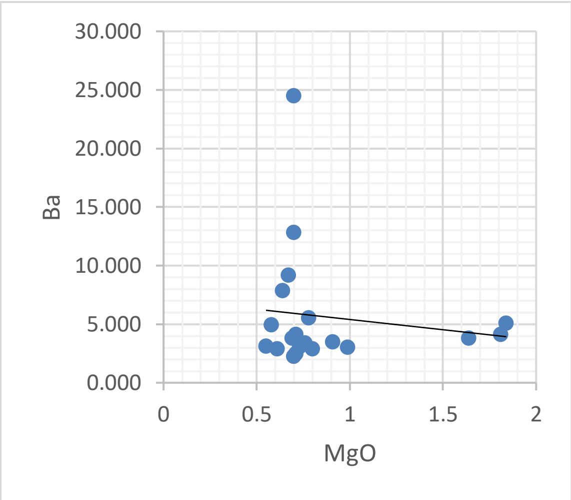

Zr
18.000
16.000
14.000
12.000
10.000
8.000
6.000
4.000
2.000
0.000
0
0.5
1
1.5
2
MgO

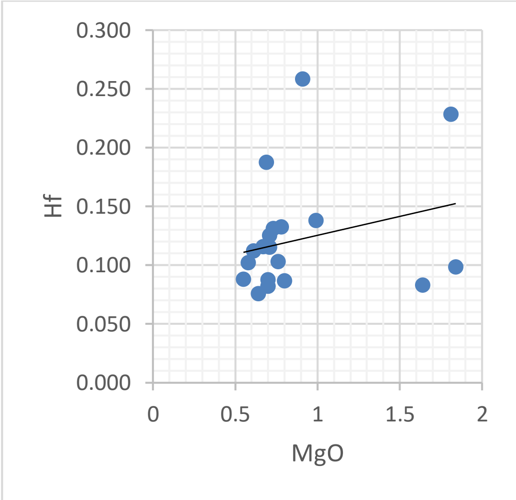
k **l**


4.000
3.500
3.000
2.500
2.000
1.500
1.000
0.500
0.000
Nb
0
0.5
1
1.5
2
MgO

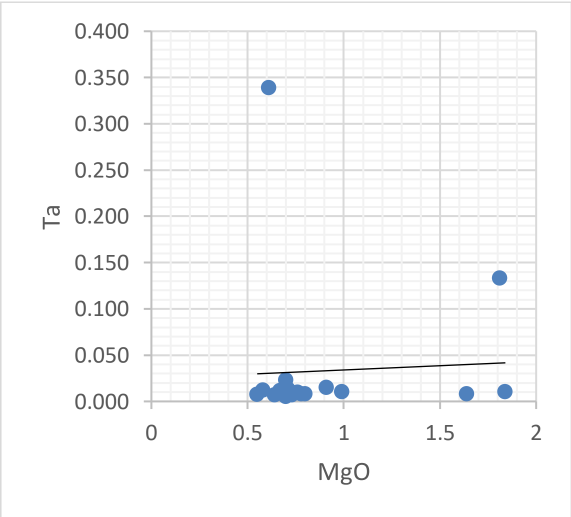

0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
Cs
0
0.5
1
1.5
2
MgO

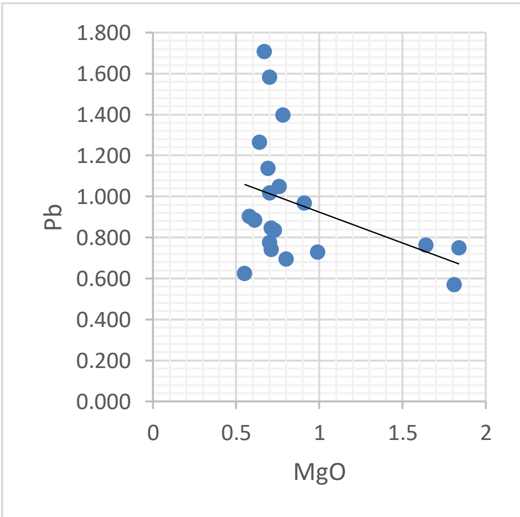
m **n**


30.000
25.000
20.000
15.000
10.000
5.000
0.000
Ba
0
0.5
1
1.5
2
MgO

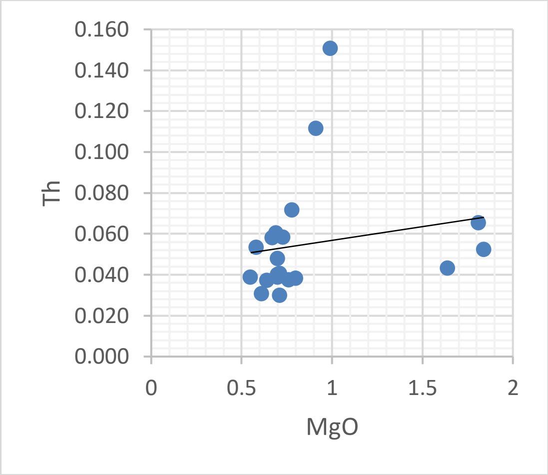

0.300
0.250
0.200
0.150
0.100
0.050
0.000
Hf
0
0.5
1
1.5
2
MgO

o **p**

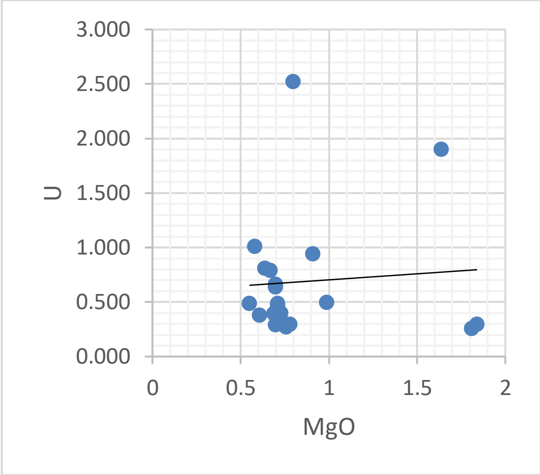

0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000
Ta
0
0.5
1
1.5
2
MgO


1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
Pb
0
0.5
1
1.5
2
MgO

q **r**



s



t

Fig. No. 09: Bivariate variation diagrams of MgO against Trace elements (after Harker, 1909)

5.6 Behaviour of Trace Elements

- **CaO with trace elements**

Trace element variation diagram of limestones have been plotted (Fig. 08) and the Harker linear variation trends of limestone indicate that most of the CaO content decrease with the increase of trace elements like V, Ni, Ga, Rb, Y, Zr and Hf which indicate strong antipathic relationships whereas Nb, Ba, and Ta appear to increase with increasing of CaO which indicates a sympathetic relationship.

Trace elements Co, Cr and Sc are almost horizontally distributed relative to CaO which does not indicate much significant relationship.

- **MgO with trace elements**

The trace elements like Ba and Pb increases with the decrease of MgO which indicates antipathic relationship whereas the rest of them, except for Zn, Ba and U (which does not show any relation) increases with the increase of MgO content which show sympathetic relationships (Fig. 09).

5.7 RARE EARTH ELEMENT (REE) GEOCHEMISTRY

The rare-earth elements have been studied intensively over the last three decades by prominent scientists all over the world. REE geochemistry presents the remarkable developments in the chemistry. The 15 elements have atomic numbers ranging from 57 for Lanthanum (La) to 71 for Lutetium (Lu). With the increasing atomic number, the electrons fill the 4f energy levels of the rare-earth elements, causing the well-known lanthanide contraction. The REE usually are trivalent (Except for Eu and Ce). Eu is both divalent and trivalent, the Eu^{+3}/Eu^{+2} ratio depending on the partial pressure of oxygen, the temperature and the bulk composition of the system. Ce is typically a trivalent cation but may be tetravalent under oxidizing condition.

The average REE concentrations are also poor (< 1ppm) except for La, Ce and Nd. The REE concentration ranges between 0.061- 5.554 ppm, totaling to 20.324 ppm with an average of 1.452ppm and exhibits the ratios; La/Nd= 1.179; Pr/Sm= 1.172; ∑La-Eu/ ∑Gd-Lu, Y= ; Ce/La= 0.971 and (Ce+ La)/Y= 2.477.

The REE data of the present study as compared with that of sedimentary limestones and carbonatites from various regions of India & various regions of the world are shown in Table-2 & 3. The REE concentration in carbonatites usually shows higher values. The graphical representation of the REE vs. atomic number for limestones from the study area along with comparison of other sedimentary limestones and carbonatites (Fig. No.4) shows a striking difference in the abundance among the REE.

The REE pattern of limestones of the study area (Fig. No. 4) is similar to that of sedimentary limestone of the Russian platform and Borra region in the Eastern Ghats in India. The curve of the carbonatites from Mbeya, Sangu complex and Kaiserstuhl does not compare with that of the limestones of the study area because of their higher enrichment of REE abundances and show intensive peaks of REE pattern. This indicates that the present limestones of the study area are of Sedimentary origin.

The REE+Y elemental concentrations of the samples were normalized with Post Archaen Australian Shale (PAAS) values reported by Pourmand et al. (2012) (Fig.No.5). The REE+Y patterns of the samples show LREE depletion with nearly flat pattern, which is typical of modern as well as ancient oceans with REE abundances ranging from 0.02X to 0.9X compared to PAAS. The anomalies are calculated as La/La*= LaSN/ (3PrSN-2NdSN) (SN= Shale Normalized), Eu/Eu*= (EuSN/[SmSN*GdSN] ^0.5. As suggested by Bau and Dulski (1996), we express Ce anomaly as [(Pr/Pr*)SN= PrSN / (0.5CeSN +0.5NdSN)] to avoid the influences of anomalous La content. The average total REE content of the samples is 20.31 ppm. The samples show both positive and negative Eu anomaly. Positive Eu anomalies may result from the interference of barium oxide during ICP-MS analysis (Jarvis et al., 1989). Although our samples have high barium content, lack of positive correlation between Ba and Eu anomaly rules out this possibility. The samples also show positive La anomalies with a mean value of 1.3. All samples show negative Ce anomaly.

The nature of the depositional environment of the carbonates can be determined using the relationship between specific parameters such as LREE depletion (expressed as (Sm/Yb) SN) and Eu anomaly and Y/Ho ratios. LREE depletion usually signifies a relatively small degree of continental input, and Eu anomaly would be significantly high for samples that are closer to the hydrothermal sources (Kamber and Webb, 2001). A negative relationship between LREE depletion and Y/Ho ratios A.V. Govind et al. Precambrian Research 357 (2021) and Eu anomalies suggests that among the sampled carbonates, samples with higher Y/Ho ratios and Eu anomaly were deposited in deeper environments compared to the samples that have lower Y/Ho ratios and less prominent Eu anomaly (Fig 6 a and b).The carbonate rock samples of this study show significant positive La anomaly and an evident positive relationship between Y/Ho ratios and La anomaly. These features are indicative of their marine origin (Fig. No. 6a).

Sl. No	REE	Average
1	La	5.55
2	Ce	5.40
3	Pr	0.92
4	Nd	4.71
5	Sm	0.85
6	Eu	0.20
7	Gd	0.70
8	Tb	0.11
9	Dy	0.72
10	Ho	0.16
11	Er	0.46
12	Tm	0.06
13	Yb	0.41
14	Lu	0.06
15	ΣREE	20. 32

Table No. 09: Average of Rare Earth Elements

												Ho	Er	Tm	Yb	Lu
Carbonatites	Panda Hill, Mbeya, Tanganyika	94.5	181.0	272.0	66.5	282.0	46.0	14.3	34.0	11	…	5.1	44.5	4.5	9	2.4
	Sangu complex, Tanganyika	38.0	76	391	25	94	18	6.7	16.7	25	…	2.05	4.5	0.53	1.5	…
Limestones from various regions (A.T. Rao et al., 1988)	Russian platform (116 samples)	23.0	10	20	2.5	9	2.1	…	2.7	…	2.5	…	5.7	…	1.6	…
	Russian platform (11205 samples)	3.8	4.1	6.5	1.7	4.6	1.4	∑Eu+Gd= 1.2		…	0.8	…	0.4	…	0.03	…
	Borra region India	13.6	3.2	8.8	2.4	2.0	1.0	0.27	0.40	0.08	0.38	0.14	0.24	0.11	0.34	0.10
Limestones from Phek District	Weziho, Shatüza, Laruri, Phokhungri, New Thewati, Zhipu&Mokie	4.4	5.55	5.40	0.92	4.71	0.85	0.20	0.70	0.11	0.72	0.16	0.46	0.06	0.41	0.06

Table No. 10: Comparison of the average REE ratios of Phek limestones to that of sedimentary limestones and carbonatites reported elsewhere (After Rao et al., 1988)

Ratio		La/Nd	Pr/Sm	∑La-Eu/ ∑Gd-Lu,Y	Ce/La	(Ce+La)/Y
Limestones from various regions	Russian Platform (116 Samples)	1.11	1.19	1.40	2.00	1.30
	11,205 samples from Russian platform	0.89	1.21	2.81	1.58	2.79
	White limestone from Borra region in the Eastern Ghats	1.60	2.40	1.13	2.75	0.87
Carbonatites	Panda Hill, Mbeya, Tanganyika	0.64	1.45	4.92	1.50	4.79
	Sangu complex, Tanganyika	0.81	1.39	9.28	5.14	12.29
Study of Limestones from Phek District	Studied samples	1.19	1.08	2.49	0.97	2.48

Table No. 11: REE ratios of Phek limestones in comparison to the sedimentary limestones and carbonatites (After Rao et al., 1988)

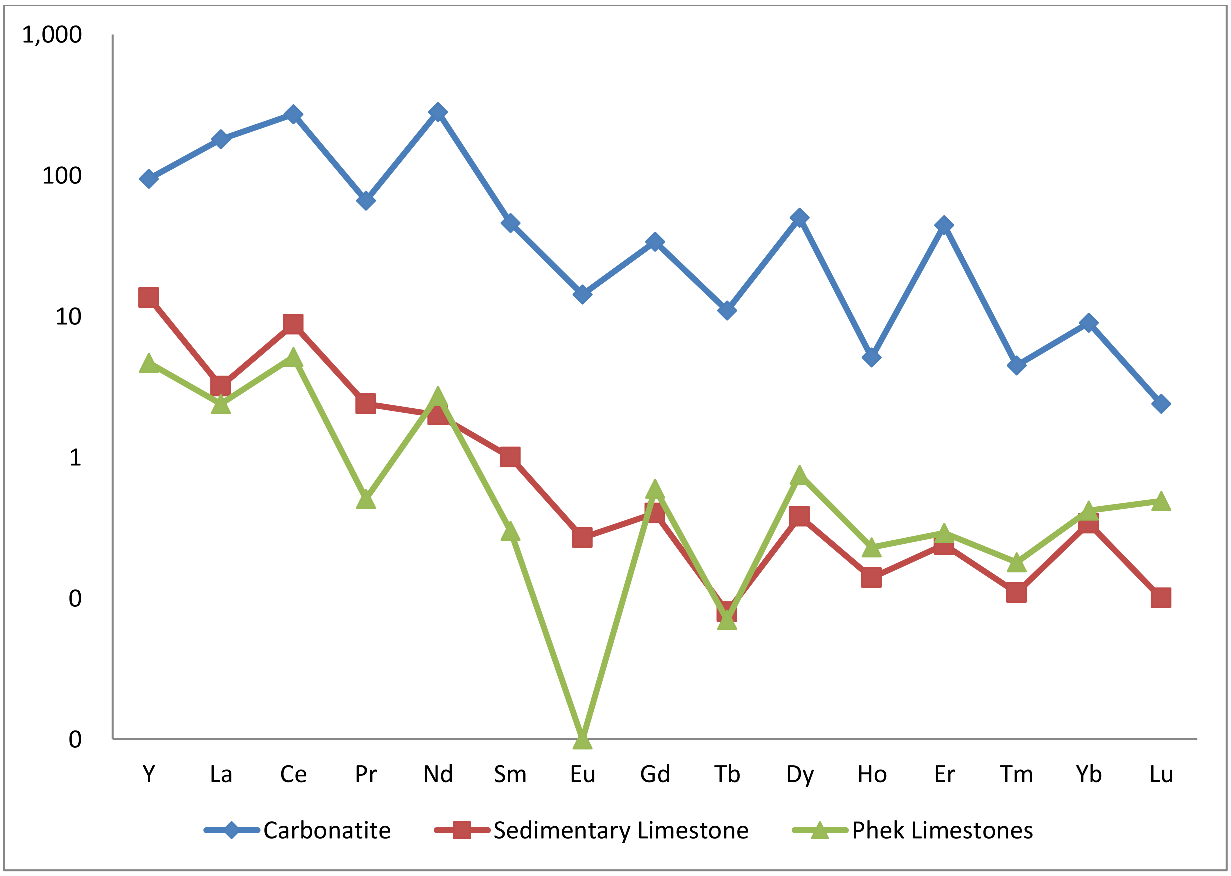


Fig. No. 10: Average REE abundances vs. Atomic Number for the Phek limestones with a comparison of other sedimentary limestones and carbonatites (After Rao et al., 1988).

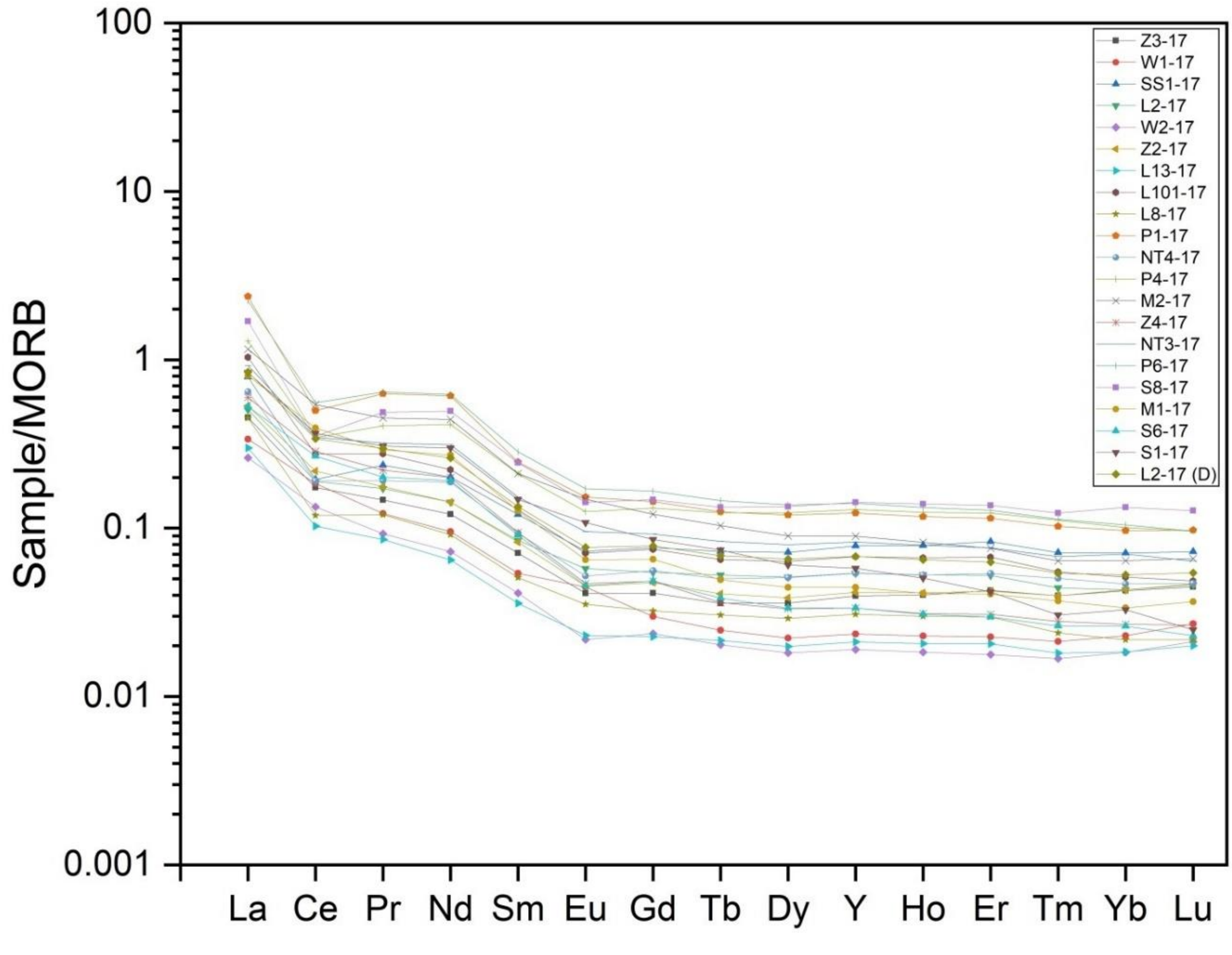
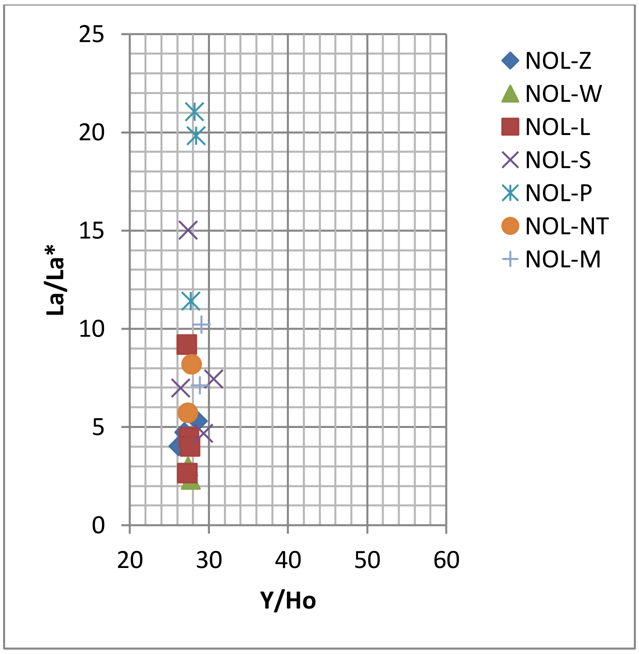
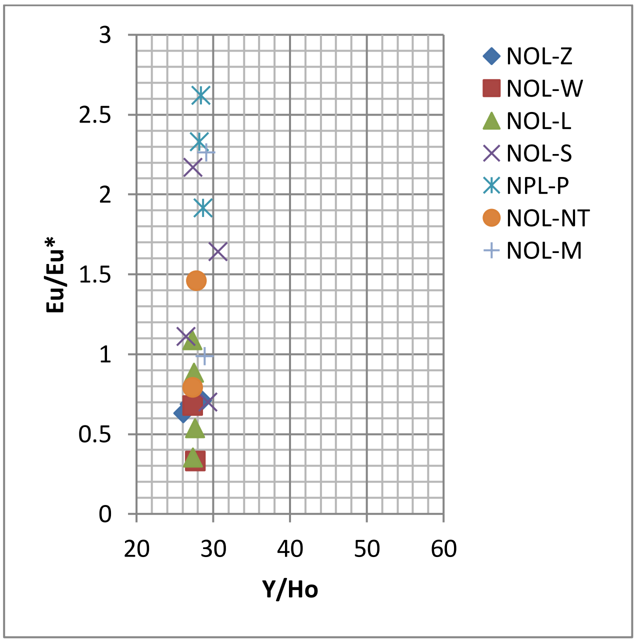


Fig. No. 11: Y+ REE MORB PAAS normalized (normalization values proposed by Pourmand et al., 2012) REE+Y plot for the carbonates. Most of the samples show depleted LREE, flattened HREE patterns, positive Y and La anomalies.

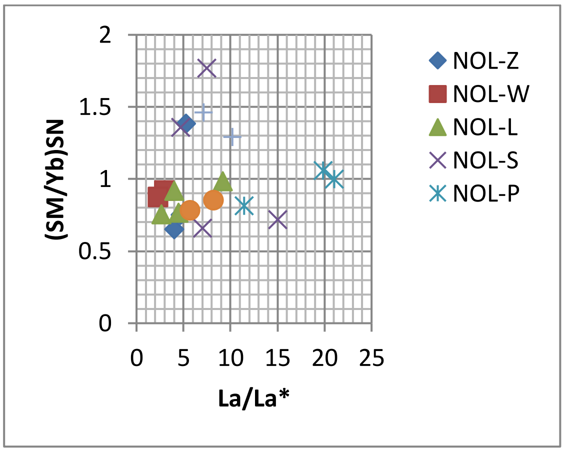


a

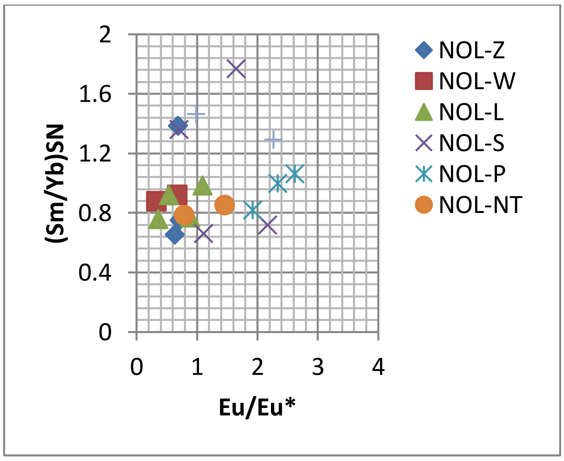


b

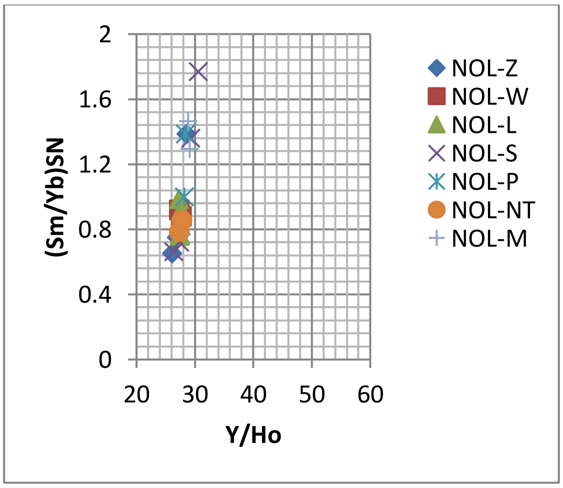
Fig.No. 12: (a) The positive correlation between La anomaly and Y/Ho ratios; both are typical of marine environments, other Archean carbonate deposits also show the same linear relationship between these ratios. (b) Limestones from Phek District show a positive correlation between Eu anomaly and Y/Ho suggesting the presence of strong hydrothermal influence. (After Allwood et al., 2010 and Kamber and Webb, 2001)



a



b



c

Fig.No. 13: Limestones from Phek District show a negative correlation in (a) LREE depletion expressed as (Sm/Yb)SN vs La/La* ratios (b) (Sm/Yb)SN vs Eu anomaly and (c) (Sm/Yb)SN vs Y/Ho anomaly. Similar relationships are observed for Campbellrand carbonates data as reported by Kamber and Webb, (2001).

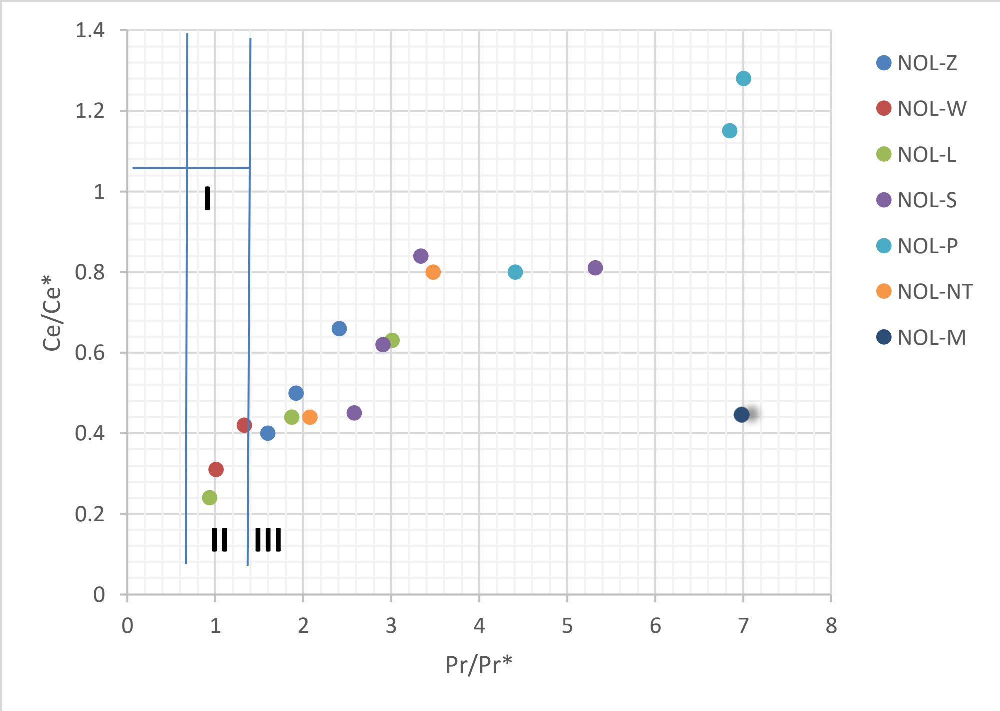
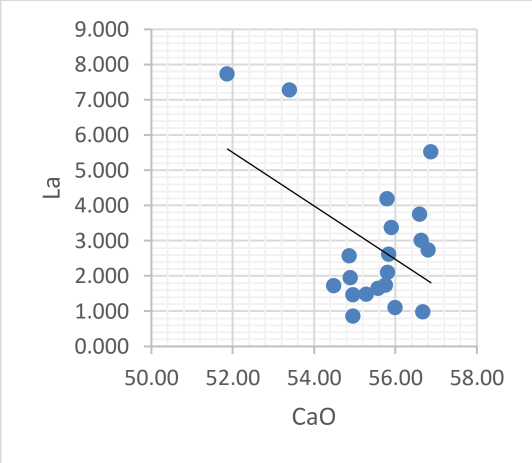
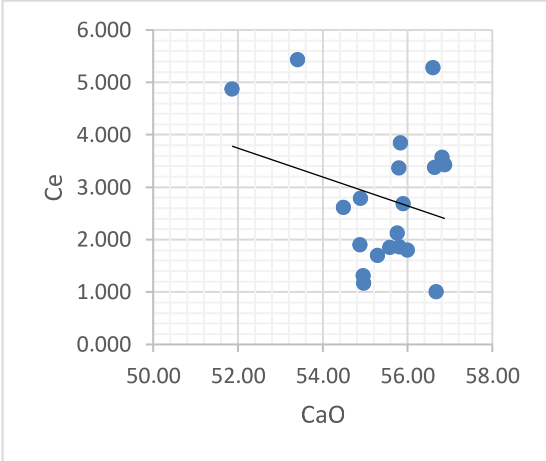
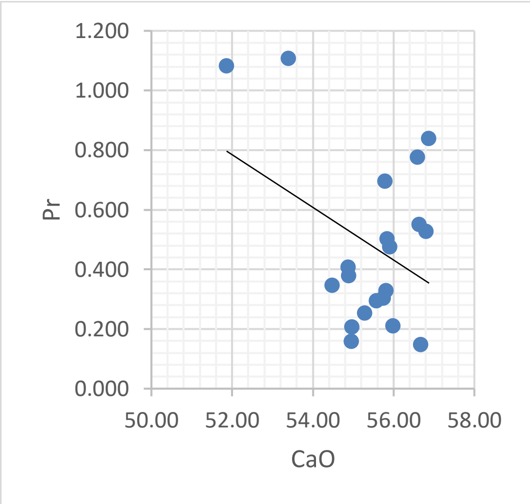


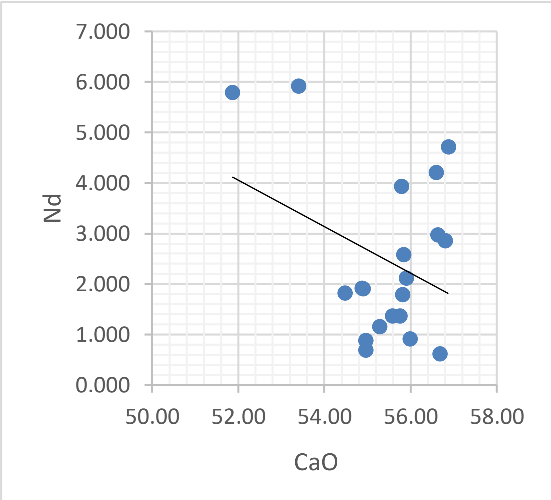
Fig.No. 14: Plot proposed by Bau and Dulski, (1996) to represent the Ce anomaly without the influence of La content. Ce anomaly is expressed as [(Pr/ Pr*)SN=PrSN / (0.5CeSN +0.5NdSN)]. Field I: samples with neither Ce anomaly nor La anomaly. Field II: samples with positive La anomaly and no Ce anomaly, Field III: samples with negative Ce anomaly (Only samples with Pr/Pr* >1.1 are considered to have a negative Ce anomaly). Most of the samples fall under this field indicating the presence of oxygen. Among the samples analysed, only 3 show positive Ce anomaly.


9.000
8.000
7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
La
50.00
52.00
54.00
56.00
58.00
CaO

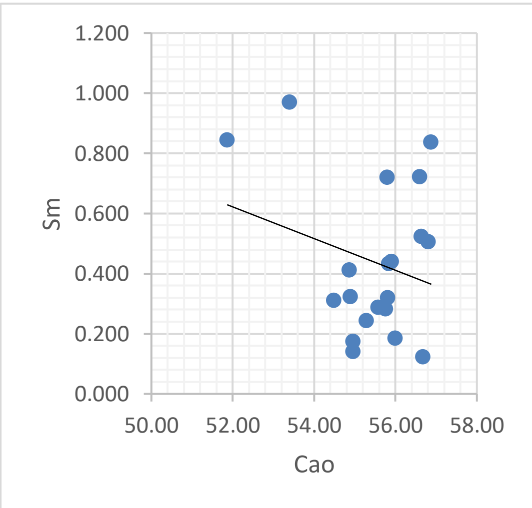

6.000
5.000
4.000
3.000
2.000
1.000
0.000
Ce
50.00
52.00
54.00
56.00
58.00
CaO

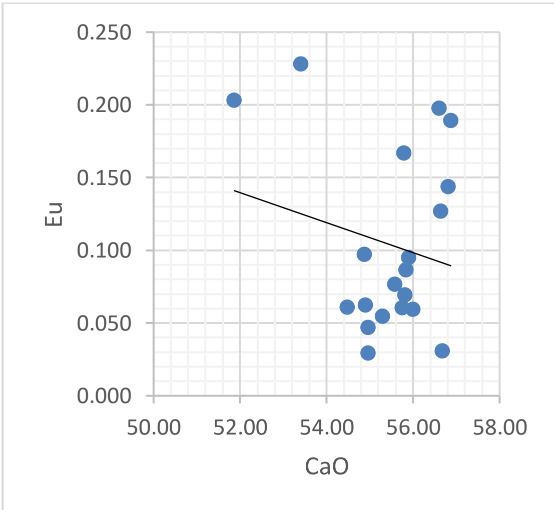
a **b**


1.200
1.000
0.800
0.600
0.400
0.200
0.000
Pr
50.00
52.00
54.00
56.00
58.00
CaO

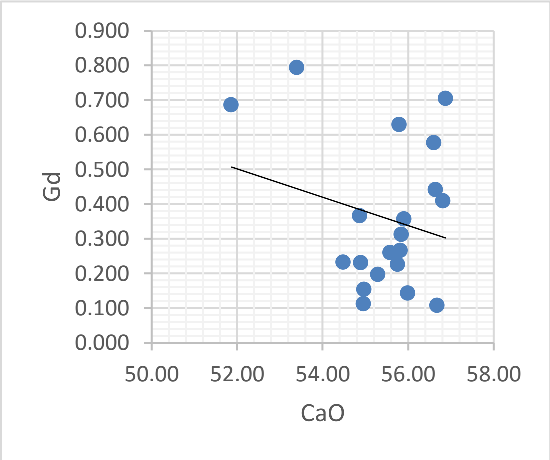

7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
Nd
50.00
52.00
54.00
56.00
58.00
CaO

c **d**


1.200
1.000
0.800
0.600
0.400
0.200
0.000
Sm
50.00
52.00
54.00
56.00
58.00
Cao


0.250
0.200
0.150
0.100
0.050
0.000
Eu
50.00
52.00
54.00
56.00
58.00
CaO

e **f**



Gd
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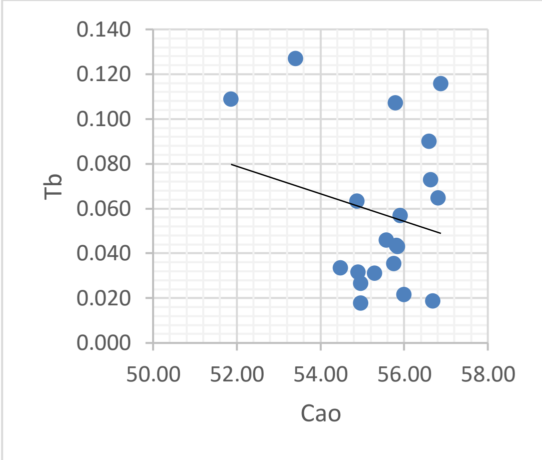
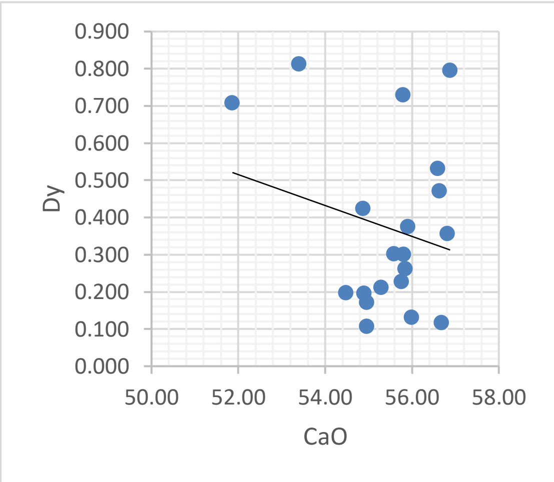
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
50.00
52.00
54.00
56.00
58.00
CaO

g



Tb
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0.000
50.00
52.00
54.00
56.00
58.00
Cao

h



Dy
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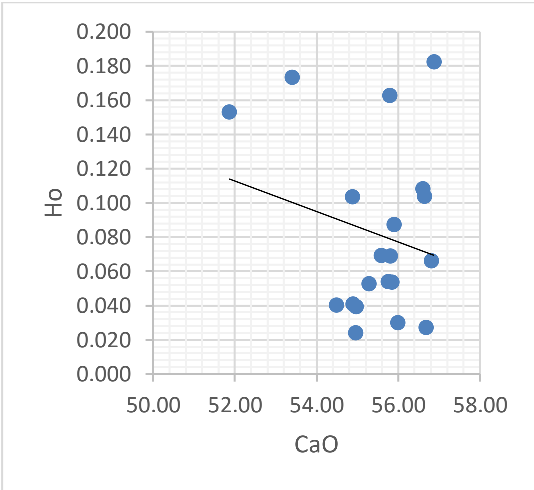
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
50.00
52.00
54.00
56.00
58.00
CaO

i



Ho
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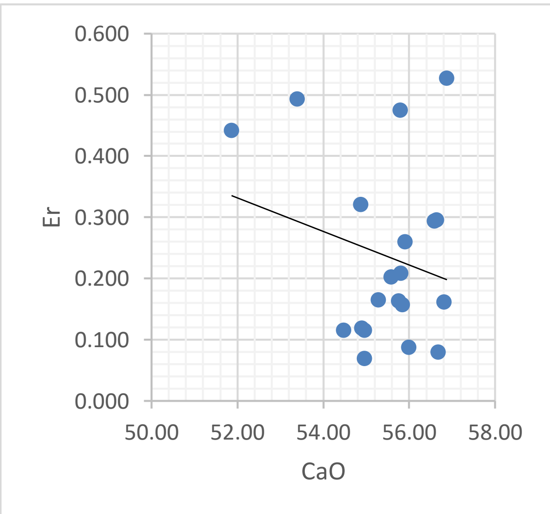
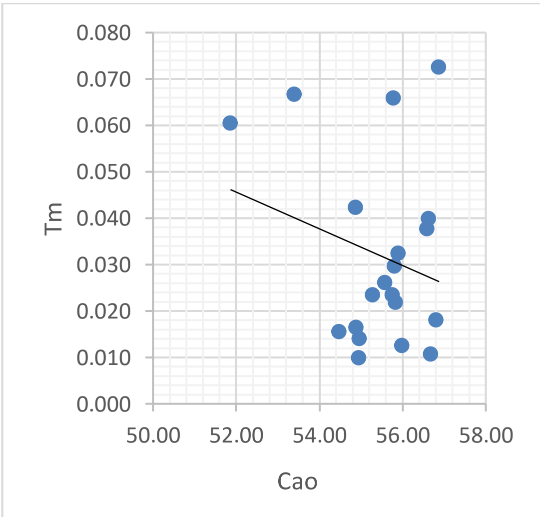
0.180
0.160
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0.000
50.00
52.00
54.00
56.00
58.00
CaO

j



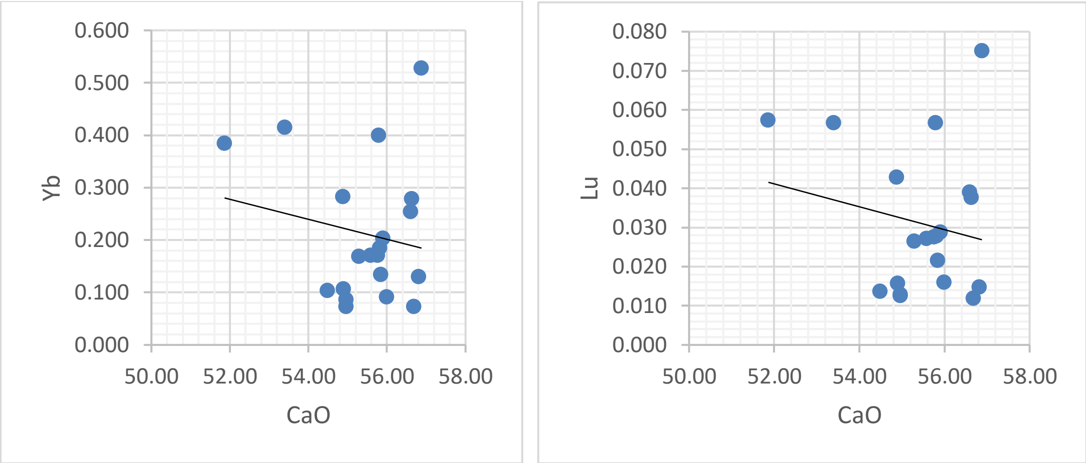
Er
0.600
0.500
0.400
0.300
0.200
0.100
0.000
50.00
52.00
54.00
56.00
58.00
CaO

k



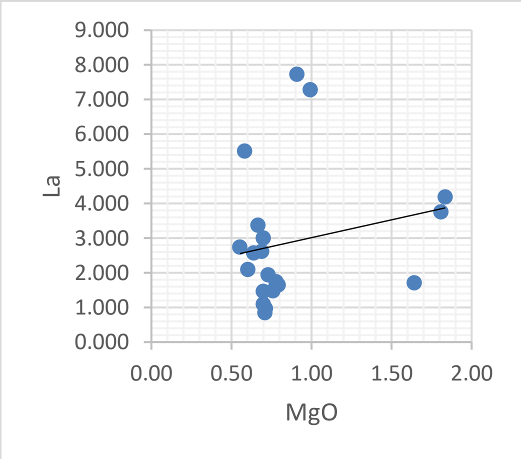
Tm
0.080
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
50.00
52.00
54.00
56.00
58.00
Cao

l

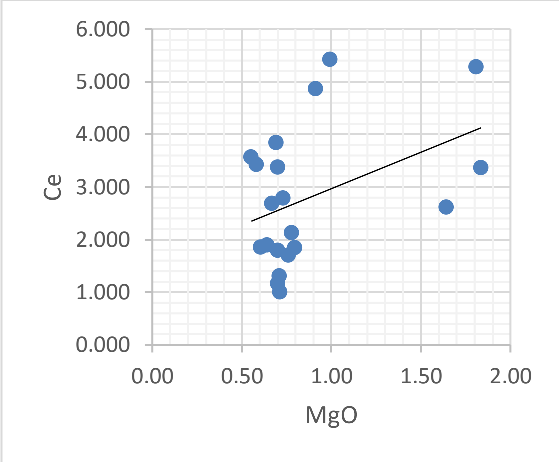


m **n**

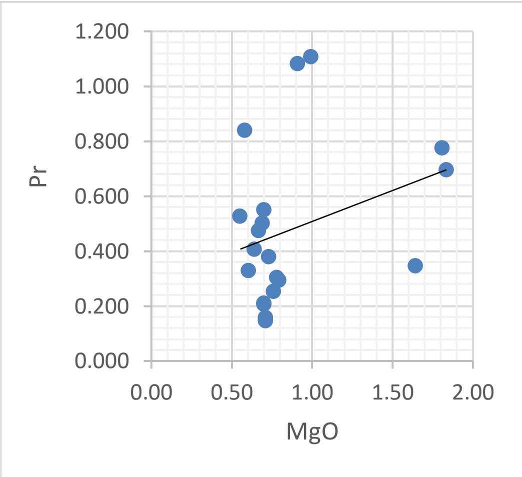
Fig. No. 15: Bivariate variation diagrams of CaO against Rare Earth elements (after Harker, 1909)


9.000
8.000
7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
La
0.00
0.50
1.00
1.50
2.00
MgO

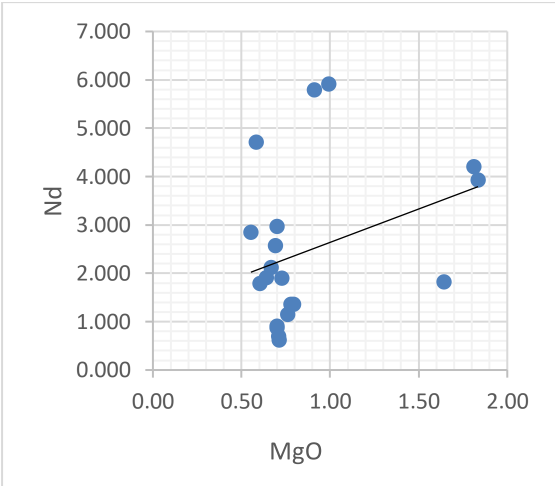
a


6.000
5.000
4.000
3.000
2.000
1.000
0.000
Ce
0.00
0.50
1.00
1.50
2.00
MgO

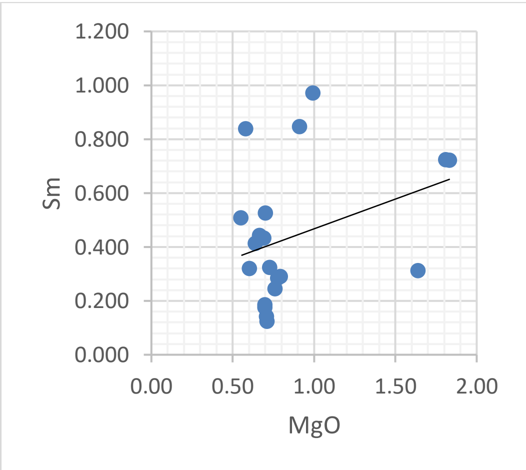
b


1.200
1.000
0.800
0.600
0.400
0.200
0.000
Pr
0.00
0.50
1.00
1.50
2.00
MgO

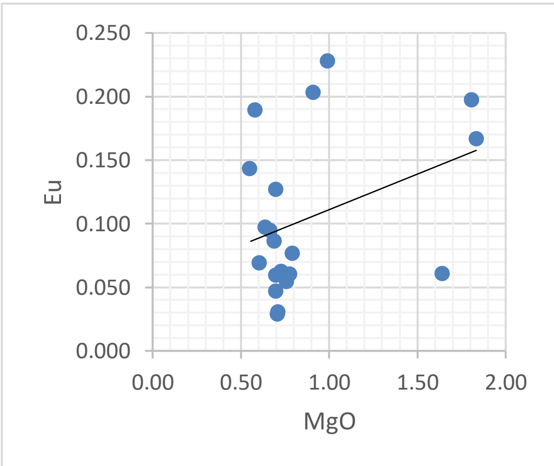
c


7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
Nd
0.00
0.50
1.00
1.50
2.00
MgO

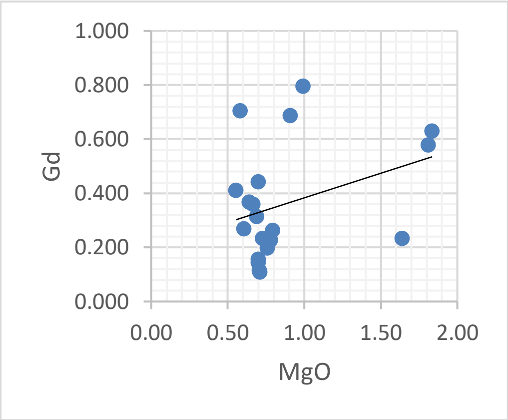
d


1.200
1.000
0.800
0.600
0.400
0.200
0.000
Sm
0.00
0.50
1.00
1.50
2.00
MgO

e


0.250
0.200
0.150
0.100
0.050
0.000
Eu
0.00
0.50
1.00
1.50
2.00
MgO

f


Gd
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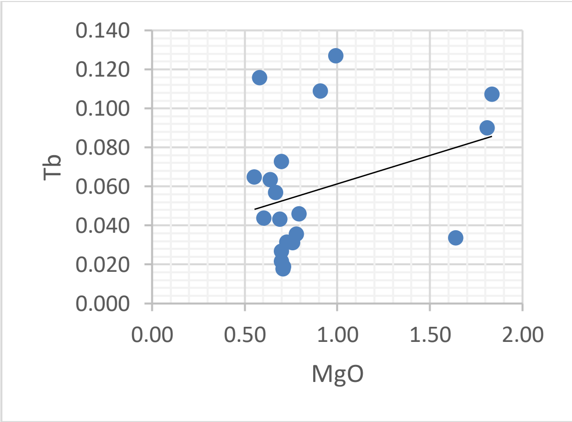
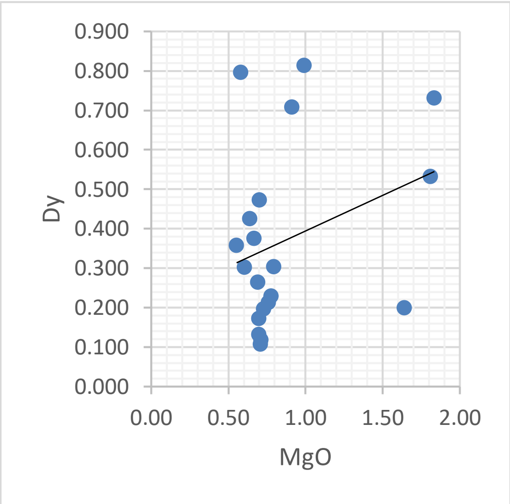
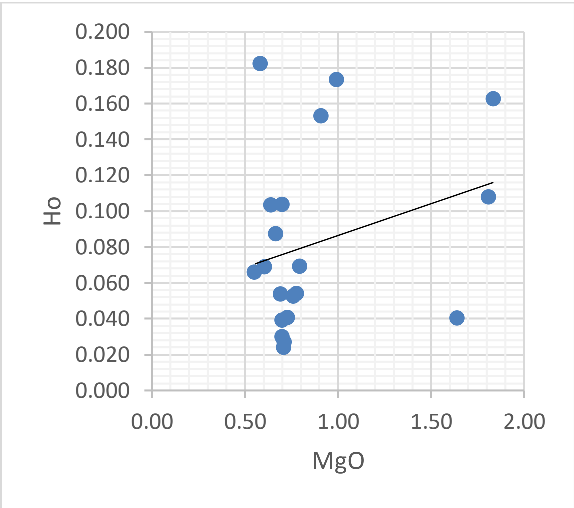
0.800
0.600
0.400
0.200
0.000
0.00
0.50
1.00
1.50
2.00
MgO

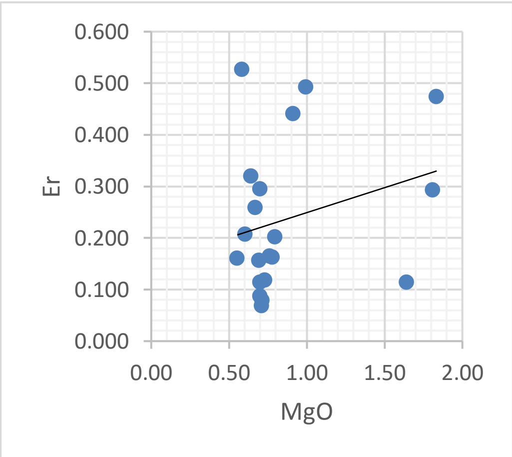

Tb
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0.000
0.00
0.50
1.00
1.50
2.00
MgO

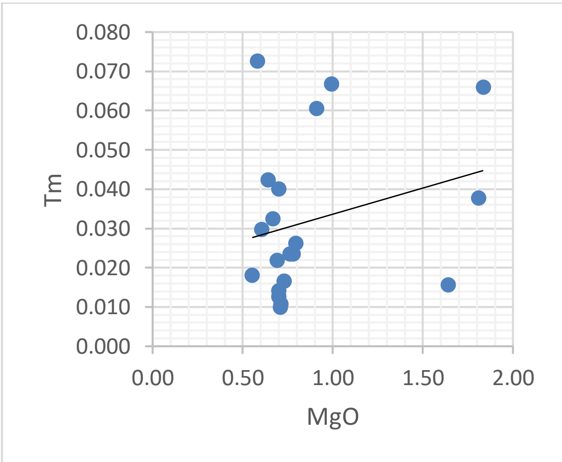
g **h**


Dy
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0.00
0.50
1.00
1.50
2.00
MgO

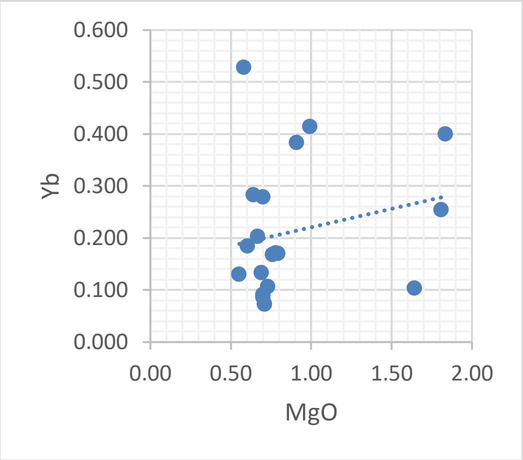

Ho
0.200
0.180
0.160
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0.000
0.00
0.50
1.00
1.50
2.00
MgO

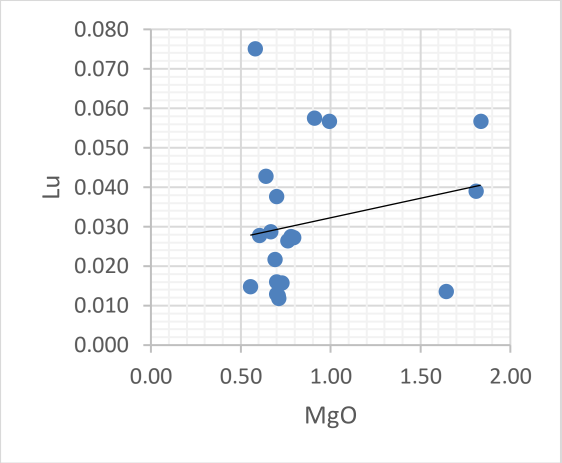
i **j**


Er
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0.00
0.50
1.00
1.50
2.00
MgO


Tm
0.080
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
0.00
0.50
1.00
1.50
2.00
MgO

k **l**





m **n**

Fig. No. 16: Bivariate variation diagrams of CaO against Rare Earth elements (after Harker, 1909)

5.8 BEHAVIOUR OF REE

- **CaO versus REE**

Almost all the Rare Earth Elements increases with the decrease of carbon content which show strong antipathetic relationship whereas Pr and Nd show a faint increase with the increase of the silica which show antipathic relationship. (Fig. 15).

- **MgO versus REE**

All the RE elements like La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb show a decrease with an increase in MgO content which indicates strong sympathetic relationships (Fig. 16).

The evidences reported from the behaviours of CaO, SiO_2 and MgO against Major, Trace and REE strongly points to the fact that the carbonates found as rootless pockets are emplaced only after the obduction of the ophiolites. In other words, the emplacement of carbonates took place with the production of a melange.

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CHAPTER-VI

DISCUSSION

This chapter focuses on the genesis and economic viability of limestones from the study area based on their field relationships, petrography and geochemical evidences.

The following major lithological units have been identified in the Naga Ophilite Belt based on the field relations: mafic volcanics(basalt and spilites), ultramafic complex (peridotites and cumulates), mafic Cumulates (gabbros), plagiogranites and and associated sediments (cherts, limestones and conglomerate etc).

The limestone deposits comes under associated sediments of NOB. The major limestone deposits are exposed at Wazeho, Shatüza, Laruri, Phokhungri, New Thewati, Zhipu and Mokie in Phek District, Nagaland. They differ largely in color, texture, hardness and durability from one place to another. Most of the deposits are massive and the rock was affected by tectonic activities. The occurrences of limestones are discussed below as per field observations.

Limestone deposits occurring as (a) tectonic slices in Disang Formation (b) Limestone associated with basalt, chert, serpentinite and phyllite- quartzites in various parts of the study area of the Ophiolite Belt of Nagaland. Field evidences clearly demonstrate that the limestones occur as a cluster of megalensoid bodies, which are an essential feature of mélanges in the Naga Ophiolite Belt.

The Limestone deposits of Wazeho lies on the Western margin of the Ophiolite belt and is in tectonic contact with the Disangs on its West. The associated rock types in the area are phyllite, chert, mafic volcanics and minor serpentinites. These have a general NE-SW strike and dip to Northwest. The limestone deposit spread over an area of approximately 0.5 km. It occurs in linear fashion having a length of 570m, and thickness varying from 5m - 20m.

Altogether eight numbers of detached limestone pockets have been located all along the length of the Shatüza- Zepuhu ridge. Of these eight pockets, five located along the ridge from North to South. The remaining three pockets lies outside the area. All the seven pockets are numbered as 1 to 7 and they together are termed as "Shatüza Limestone Deposit." It occurs in NE strike continuation of the Wazeho deposit. The limestone pockets are associated with Volcanics, Serpentinite and Chert.

The limestone deposits of Phokhungri are found in the form of rootless pockets and exhibit fine grained, whitish to grayish in colour with shades of dark bands and shows physical contact with Black marble. A lensoid body of ash colored limestone deposit is found in the East of New Thewati. Further, the limestones occur in the form of detached pockets are scattered over an area of about 2.5km, with the association of ultramafics (serpentinite) and volcanics along the Zhipu- Mokie road. Altogether seven numbers of pockets were record on the N-W and SW and SE of Mokie. The Limestone of Zhipu occur as a drifting deposit along Zhipu- Moki road. They are white, very fine grained and crystalline in nature. Number of Limestone pockets are also located at Zepuhu range, situated at Northern part of Zhipu Village.

The limestone deposits occur in the form of detached pockets are scattered over an area of about 2.5km, with the association of ultramafics and volcanics at Mokie and shows a contact with serpentinite. In general, they are white, whitish grey to dark grey in color, hard massive, compact and crystalline in nature. Altogether seven numbers of pockets were record on the N-W and SW and SE of Mokie. Out of these, the pocket one is located 1.5km Northwest of Mokie is considered to be the main band/pocket. Development of fractures, joints is filled with calcite veins, which are common in this area.

Total reserves of limestone deposits to be about 50 million tons from Wazeho, Shatüza, Mokie and other areas in Phek district of Nagaland (Agrawal (1978). The exotic blocks of limestones are found in the melange zone where they are mixed with basalt which is of the pre-existing rock of ocean basin. They are the product of tectonic activity due to which they do not show any continuity. The subduction caused by tectonic activity dumped the limestones into the ocean where they were mixed with the basaltic material whereby causing a burnt effect to be seen in on the limestones as a result of the contact of the two. The exotic limestones are generally reported to be of Maestrichtian age.

Petrographic studies show that the limestones vary in color from greyish white to grey and are mostly composed of calcite with subordinate amount of dolomite and minor crystals of diopside, chlorite, apatite, quartz, and iron are observed in thin sections. The calcite grains show the usual change of relief, which is referred to as “Twinkling” and the colorless calcite grains are seen with irregular boundary, indicating the rocks to have undergone recrystallization. Calcite shows prominent twinning under crossed polar which is to be considered useful in distinguishing calcite from dolomite. The sub-hedral calcite grains showing perfect rhombohedral cleavage (usually in 3 sets) observed under crossed polar.

Dolomite occurs as tabular crystals, often with granular and massive with calcite. It shows white, grey to pink reddish white, brownish white, colorless in transmitted light, three sets of cleavage but not at right angles. Under a microscope dolomite and calcite look similar, but thin sections, the brighter mineral grains are dolomite and the darker grains are calcite. In thin section, chlorite appears as flakes with irregular birefringence and greenish pleochroism either as radiating aggregates filling cavities or as alteration products of minerals such as biotite, etc. Quartz occurs as small anhedral grains within and in between feldspar grain boundaries and also encloses plagioclase laths. Apatite occurs as tabular, prismatic crystals, transparent to glowing, usually green, yellow, brown in colour, indistinct cleavage, pleochroism is blue, yellow to colorless. Iron minerals occurs as anhedral grains along the borders of other minerals. Magnetite is black in colour with a metallic lustre in reflected light whereas hematite is steel grey to black with a tendency to a marginal red; some are red and translucent.

Geochemical analysis of the limestones from the study area indicates that the limestones have an average CaO composition of 55.429%; MgO and SiO_2 less than 1% and 3%. It also shows low concentrations of trace elements like Cr, Co, and Ni and REE like La, Ce, Pr, Nd, Sm, Er, Gd, Tb, Dy, Ho, Yb and Lu when compared to that of carbonatites of igneous origin from different regions in India (Table 2 & 3 & Fig. 4). Further, the ratios of La/Nd, Pr/Sm. Ce/la and Ce+La/Y values from the study area coincide with the ratios of limestones of sedimentary origin from different regions of India and Russia.

The presence of Sr^{2+} and Zn^{2+} in a large amount is of considerable geochemical interest (Table No. 05 & 06). Normally Sr accompanies Ca in minerals and rocks of both igneous and sedimentary origin, although the substitution may not be as extensive in the case of calcite as in aragonite (Deer et al., 1962). The significantly large amount of Sr in the sample is perhaps an indication of the marine origin of the sediments and/or recrystallization of calcite from aragonite (Narasinga Rao, 1971).

The trace element abundances in carbonate rocks is a concern to understand the chemical evolution of the Archean ocean-atmosphere system. REEs and other conservative trace element abundances and their ratios are help in constraining the early earth processes (Bau and Dulski, 1996; Kamber et al., 2004; Van Kranendonk et al., 2003; Webb and Kamber, 2000; Webb et al., 2009; Allwood et al., 2010). The ability for complexation of REEs with carbonates varies with their atomic number. HREEs have a higher tendency to form complexes with carbonate ions, which results in typical HREE enriched pattern in marine chemical sediments (Bolhar et al., 2004). There are several parameters, such as REE+Y abundance, Y/Ho ratio, Eu, La, and Ce anomalies that are employed to identify sources and decipher physico-chemical conditions of deposition. Banner et al. (1988) have shown that the REEs, as well as Nd isotopes, remain largely unaltered by diagenetic processes.

Terakado and Masuda, (1988) and Zhong and Mucci, (1995) have reported that in carbonates, the REEs replace Ca2+ in the lattice which explains the conservative nature of REEs. The REE+Y patterns of our samples are similar to those of previously reported marine sediment REE+Y patterns representing Archean marine environment, i.e., LREE depleted and HREE enriched pattern with positive Eu and Y anomalies and varying Ce anomalies. The total REE content, when plotted with Sc and Th, did not show any correlation; this argues against the possibility of significant detrital contamination of REEs. All the anomalies exhibited by the samples, such as La/La*, Y/Y* Eu/Eu* are well correlated with each other, which is suggestive of REE+Y patterns preserving the primary marine nature.

According to Bolhar et al. (2015), Eu and Ce are most susceptible to post-depositional changes among REEs, as they can be mobilized in presence of fluids. This possibility can be verified by plotting these elements with their neighboring REEs. The plots of Ce vs. La and Eu vs. Gd showed a linear relationship between the pairs, thereby ruling out the possibility of considerable post-depositional changes in Eu and Ce concentration. The PAAS normalized REE+Y patterns (Fig. No. 11) of the samples show slightly LREE depleted HREE enriched trend as well as super chondritic Y/Ho ratios. Also seen are strong La and Eu anomalies and presence of negative Ce anomaly in most samples, which are typical to that of modern marine environment (Allwood et al., 2010; Kamber and Webb, 2001; Fryer, 1977a, 1977b).

Y/Ho ratio serves as a useful tool in understanding the nature of the depositional environment. Generally, Y and Ho show similar characteristics, hence their ratio remains almost the same in various geochemical reservoirs such as mantle and crust. But in aqueous systems and in their precipitates, Y and Ho often behave differently, Ho Fig. No. 12 (a & b) The positive correlation between La anomaly and Y/Ho ratios; both are typical of marine environments (b) The carbonates of the study area show a positive correlation between Eu anomaly and Y/Ho suggesting the presence of strong hydrothermal influence in the Archean oceans. A similar trend is seen in other Archean carbonates from different cratons.

The limestone samples of this study show significant positive La anomaly (mean = 1.30) and an evident positive relationship between Y/Ho ratios and La anomaly (R2 =0.57). These features are indicative of their marine origin (Fig. No. 12a & b).

The carbonate samples with less radiogenic Sr isotopic compositions also have well preserved C isotopic compositions, whereas the higher radiogenic 87Sr/86Sri values correspond to depleted δ13C values which suggest that the radiogenic Sr isotopic compositions could be due to lowgrade metamorphism (Siahi et al., 2018; Veizer et al., 1990). Studies have shown that granites and gneisses show low 87Sr/86Sr values as a result of the early loss of Rb caused by metamorphic fluid flow (Jayananda et al., 2015). Whereas, intercalated silicate phases such as clays and micas in carbonates with high Rb/Sr ratios release radiogenic Sr during metamorphism, which was readily accommodated in the carbonates resulting in elevated 87Sr/86Sr ratios.

According to Burns et al. (1994) and Derry (2010), high-temperature diagenetic processes as well as larger water-rock ratios reduce the Sr concentrations, but also result in elevated Mn/Sr ratios, Fe, Mn concentrations and considerably alters the Rb/Sr and 87Sr/86Sr in the limestones. Although in the present study, most of the samples with high Mn contents and low Sr exhibit primary, oceanwater-like 87Sr/86Sr initial ratios, yet we cannot rule out the possibility of diagenetic alteration. The primary nature of Sr isotopic compositions can also be justified by correlating with Y/Ho ratios (Fig. 13c). The samples, with, low 87Sr/86Sri ratios and considerably elevated Y/Ho ratios, are interpreted to be of marine character. The same trend can be seen while correlating with other typical marine REE+Y attributes such as Eu and La anomalies.

The nature of the depositional environment of the carbonates (limestones) can be determined using the relationship between specific parameters such as LREE depletion (expressed as (Sm/Yb) SN) and Eu anomaly and Y/Ho ratios. LREE depletion usually signifies a relatively small degree of continental input, and Eu anomaly would be significantly high for samples that are closer to the hydrothermal sources (Kamber and Webb, 2001). A negative relationship between LREE depletion and Y/Ho ratios and Eu anomalies suggests that among the sampled carbonates, samples with higher Y/Ho ratios and Eu anomaly were deposited in deeper environments compared to the samples that have lower Y/Ho ratios and less prominent Eu anomaly (Fig No. 12b). The negative correlation of LREE depletion (Sm/Yb)SN) with Y/Ho, Eu/Eu*and La/La*(Fig. 8a, b and c) indicates that the samples with better preserved marine character have higher Y/Ho, Eu/Eu*, La/La* anomalies and more depleted LREEs, similar to the Campbellrand platform carbonates of the Kaapvaal Craton (Kamber and Webb, 2001).

The samples having comparatively less prominent Eu and La anomalies, less depleted LREEs, and chondrite like Y/Ho ratios may have been deposited at shallower depths with inputs from continental sources. Samples with high positive Eu anomalies and Y/Ho ratios also have positive Nd values, typical of depleted mantle, which further affirms that these carbonates were deposited at greater depth and farther away from the continent in the vicinity of a hydrothermal source.

Samples from, Bheemasamudra, and Kalche with less prominent Eu anomalies, chondritic or sub-chondritic Y/Ho ratios and insignificant La anomalies represent carbonates deposited in these shallower marine settings. By contrast, samples from Yerekatte and Kenkere show features of moderately deeper depositional environments and samples from Gundikere and Arbailghat have the most prominent Eu and La anomalies, as well as high Y/Ho ratios and much-depleted LREEs, implying that their deposition occurred at deeper parts of the shelf, close to centers of submarine volcanism and hydrothermal activity.

The possible existence of small pockets of free oxygen or oxygen oases was discussed by many studies in shallower protected environments of Archean oceans, where the chances of consumption of free oxygen by marine Fe (II) during banded iron formations (BIF) deposition were less, atmosphere exchange of free oxygen was also negligible (Planavsky et al., 2014; Fralick and Riding, 2015; Homann et al., 2018). The presence of oxygen in the water would influence solubility, and in turn, the abundance of redox-sensitive. The carbonates of the study area show a negative correlation in (a) LREE depletion expressed as (Sm/Yb)SN, vs Y/Ho ratios, (b) (Sm/Yb)SN vs Eu anomaly and (c) (Sm/Yb)SN vs La anomaly. Similar relationships are observed for Campbellrand carbonate data as reported by Kamber and Webb, (2001).

Plot proposed by Bau and Dulski, (1996) to represent the Ce anomaly without the influence of La content (Fig. No. 14). Ce anomaly is expressed as [(Pr/ Pr*)SN=PrSN / (0.5CeSN +0.5NdSN)]. Field I: samples with neither Ce anomaly nor La anomaly. Field II: samples with positive La anomaly and no Ce anomaly, as most of the samples fall under this field. Field III: samples with negative Ce anomaly (Only samples with Pr/Pr* >1.1 are considered to have a negative Ce anomaly). Among the samples analyzed, only 4 show negative Ce anomaly, indicating the presence of oxygen in the Neoarchean ocean (Govind et al. (2021). Under oxidizing conditions, Ce will be predominantly tetravalent; therefore, tends to be more particle reactive and gets absorbed to the surface of detrital sediments and causes negative Ce anomaly in the seawater (Bau and Dulski, 1996).

The Archean oceans are generally considered as reducing, and many studies have reported the absence of well-developed Ce anomaly in chemical sediments (Kamber et al., 2004). However, several studies have also reported the presence of a significant amount of oxygen in the waters of Archean oceans (Riding et al., 2014, Siahi et al., 2018. When we look at the Ce anomalies of carbonates of the study area, most of the samples fall under field III (Fig. No. 14) which represents “negaitve Ce anomaly and few positive La anomaly”; these samples have Pr/ Pr*=1±0.05 and Ce/Ce* < 0.95. A few samples show neither Ce anomaly nor La anomaly. However, most samples deposited at shallower depths fall under field III (Fig. 14), which represents negative Ce anomaly (considering samples with (Pr/Pr*)SN> 1.1, Ce/Ce*

The presence of oxygen in the water would influence solubility, and in turn, the abundance of redox-sensitive trace elements in the precipitated sediments (Hua et al., 2013; Robbins et al., 2016). Under oxidizing conditions, Ce will be predominantly tetravalent; therefore, tends to be more particle reactive and gets absorbed to the surface of detrital sediments and causes negative Ce anomaly in the seawater (Bau and Dulski, 1996).

The limestone played a major role in adjusting the original textural and compositional features due to marine burial characterized by compaction, recrystalliztion, pressure solution, and neomorphism. Thus, the petrographic studies indicate that the deposition of carbonate sediments took place in a calm water shallow marine basin.

The REE ratios (i.e., $(La/Ce)_N$, Ce/Ce*) as well as other immobile elemental ratios (e.g., Zr/Ti, La/Sc) of limestones are good substitutions of all depositional regimes. The average composition of the limestones deposited in various depositional environments are presented, and the open oceanic limestones are differentiated from the other groups of limestones.

Field-relations, Petrographic study surmises that the limestones of the study area are of sedimentary origin. The close association of these limestones with pelagic sediments and volcanics of the Naga Hills Ophiolite Belt suggests their deposition in an ocean basin in a fluctuating Carbon Compensation Depth regime.

Geochemical data indicates that the limestones deposits are economically viable based on average composition of CaO (55.43%) and negligible content (<1-3%) of MgO and SiO_2 which is placed above the cement grade quality as per the Indian Mineral standards.

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CHAPTER –VII

SUMMARY AND CONCLUSIONS

The study area is a part of the Naga Ophiolite Belt (NOB) and lies between the Latitude. 25° 33′40″ N to 25° 44′0″ N and longitude 94° 41′40″ E to 94°52′0″ E, It occupies an area of 329 sq. km under the Meluri sub-division of Phek District, Nagaland (NE India) and falls in the Survey of India Toposheet No. 83K/14.

The Naga Ophiolite Belt occurring along the Indo-Myanmar border forms a part of the Naga-Arakan-Yoma flysch trough of Upper Cretaceous–Middle Miocene age. This belt is tectonically sandwiched between the Nimi Formation on the east and the Disang flysch towards the west. The NOB, extending over 90 km in length along the strike with widths varying from 2-15 km, covers an area of about 1000 sq. km. The Indo-Myanmar Range (IMR) is considered the northern prolongation of the Indonesian Island Arc, which in turn is linked up northward with the eastern end of the Himalayas. Slices of the ophiolites of varying dimensions are arranged in NE-SW to N-S trending en-echelon patterns with parallel to sub-parallel tectonic inter-relations. They have not preserved in sequential order and are highly dismembered.

The ophiolites of Nagaland consist of a various mixture of igneous, sedimentary and metamorphic rocks of which the mafic and ultramafics are the main components. There is a shallow water sedimentary cover consisting of conglomerate, sandstone and shale over the ophiolites. The main litho-members of the Disang flysch are shale, slate and greywacke.

The metamorphic belt consists mostly quartzite, marble and phyllite with other members of the ophiolite, mainly mafic volcanics and ultramafics. A sequence of limestone-shale occurs as pockets and lenses close to the Disang Formation.

The major lithological units of Naga Ophiolite Belt are (1) mafic volcanics (basalts); (2) ultramafics (peridotites, pyroxenites, serpentinites); (3) mafic cumulates (gabbros); (4) plagiogranites; (5) associated sediments consist of chert, shales and limestone.

A number of limestones occur as small to large detached bands and lenses of variable dimensions found in the Naga Ophiolite Belt, and these could be broadly grouped into the following Stratigraphic categories:

ii. Limestone occurring as tectonic slices in Disang Formation within the Ophiolite: there are only minor limestone bands within the Disang near the contact with the ophiolites. A medium-sized limestone deposits has been recognized along the Pfutsero -Meluri area in the Phek District, Nagaland where the Disang is composed of shale, slate, sandstone. It is grey and pink coloured, argillaceous in nature and extends over 115m with thickness varying from 7m-10m.

iii. Limestone associated with volcanic chert of the Ophiolite suite: Limestone of this category is often closely interbedded with chert- volcanic assemblage. The following are some of the localities that reported such type:

d. Shatüza- Yisi: white to grey crystalline/massive limestone bodies of variable dimensions occur in these localities associated with chert and volcanic rocks.
e. Mokie: Three medium- sized lensoid bodies of limestones which occur within spilite and chert with strike length varying from 50 m to 100 are similar in physical and chemical characters to that of Wazeho- Satuza deposits.
f. Wazeho: several pockets of limestone of varying dimension within an area of 0.5 sq. km. This occurrence is adjacent to the contact with the Disang Formation and located SSE of Wazeho village in the western margin of Zepuhu range (2509 m). The biggest of these pockets is about 700 m x 10 m to 50 m x 50 m in size and exposed as a tectonic contact with chert.

iii. Limestone associated with metamorphic formations (phyllite- quartzite) : In this category, there are quite a few occurrences most of which contain thin partings of phyllite-quartzite. Some of the occurrences observed are as follows:

d. Laruri: non-crystalline, well bedded limestone is exposed within shale-slate-sandstone units at about 2 km NE of the Laruri village. The bands are folded, fractured showing minor slips.
e. Thewati: There are a few ash coloured limestone bands having approximate dimension of 120 m x 40 m each found at east of New

Thewati. with thin partings of phyllite. In addition to that two lensoid bodies measuring 750 m x 25 m occurs near Old Thewati. Along strike direction of this band is another band measuring 120 m x 20 m.

Aim and Objectives

The present investigation is an attempt to throw light on their genesis and economic viability of the limestones by extensive studies of field relationships, petrography and geochemistry. The following objectives were undertaken to achieve during the course of study:

* Identification of limestones and associated rocks based on field study
* Identification of mineralogical composition of limestones based on Petro-minerographic study.
* To decipher the genesis and economic viability of limestone based on rock chemistry (major oxides, trace and REE) and their petrochemical plotting.

Based on the field observation, petrography and geochemistry the present study has been presented in the form of PhD thesis, which comprises seven chapters:

Chapter I Introduction:

The first chapter gives the general information including location, physiography, climate, flora & fauna, drainage, human habitation, accessibility & communication, previous literature, and aim & scope of work.

Chapter II Geological setting:

It includes the regional and local geology, major structures and stratigraphic succession of Nagaland, and tectonic setting of NE India. Based on field and petrographic evidences, the Naga orogenic belt can be broadly divided into four distinct tectono-stratigraphic units. These are: (i) Belt of Schuppen: a sedimentary nappe of Eocene-Upper Miocene age. (ii) Disang: a thick pile of clastic flyschoid sediments dominantly argillaceous of Upper Cretaceous-Eocene age. (iii) Ophiolite: a suite of magmatic, metamorphic and marine sediments of Maestrichtian–Palaeocene age. and (iv) Nimi/Naga Metamorphics: a low-grade pelitic-psammitic and carbonate sequence of Mesozoic/Proterozoic.

Chapter III Methodology:

Various field and laboratory techniques have been adopted in this chapter to decipher the physical, optical and chemical properties of the limestones. Laboratory work adopted in the present study includes the preparation of rock thin sections for microscopic studies to identify the rocks and determine their mineral constituents. Preparation of powders for geochemical analyses for the estimation of major, trace and rare earth elements using XRF, ICP-MS, etc.

Chapter IV Field relations and Petrography:

It includes the field relations among the various rock types of the study area and their petrography and mineralogy. The limestones and associated rocks in the study area are examined and classified mainly on the basis of mode of occurrence, lithological association, field relationships and mineralogical assemblages.

The major limestone deposits are exposed at Wazeho, Shatüza, Laruri, Thewati, Zhipu and Mokie of Phek District, Nagaland. They differ largely in colour, texture, hardness and durability from one place to another. Petrographic studies affirm that the limestones are mostly composed of calcite with minor presence of dolomite, diopside, chlorite, quartz, and apatite.

Chapter VI Geochemistry:

In this chapter, major, trace and rare earth element contents of 20 limestone rock samples and their geochemical behaviour are discussed. Comparisons of the pairs of elements in the limestone are also described with the help of correlation coefficient ratios. The chemical data were processed through a number of petrochemical calculations, graphical representations to decipher the genesis and economic viability of limestones.

This chapter summarizes the work carried on the limestones of the study area based on the present investigation. Finally, the conclusions have been recorded.

The salient features of the present research work are as follows:

- The Naga Ophiolite Belt is an arcuate linear belt between the Disang flysch on its west and Nimi Formation (metamorphics) on its east, extending for a strike length of 90 km with varying width of 2 to 15 km and covers an area of about 1000 sq. km. belongs to Upper Cretaceous–Middle Miocene age.

- The major lithological units of Naga Ophiolite Belt are (1) mafic volcanics (basalts); (2) ultramafics (peridotites, pyroxenites, serpentinites); (3) mafic cumulates (gabbros); (4) plagiogranites; (5) associated sediments consist of chert, shales and limestone.

- Limestone deposits occurring as (a) tectonic slices in Disang Formation along the Pfutsero to Meluri road. (b) Limestone associated with volcanic chert at Wazeho- Shatüza- Zepuhu range (c) Limestone associated with metamorphics like phyllite- quartzite, found at Laruri: and Thewati in the study area.

- Limestones deposits occur as pockets/lenses, boulder, bedded and massive type and exotic in nature in the study area. They are hard, compact and crystalline in nature medium to fine grained. The limestone exhibit whitish to ash grey with shades of dark color.

- Petrographic studies show that they are composed mainly of calcite, dolomite and quartz with occasional presence of diopside, chlorite and apatite.

- Total reserves of limestone deposits to be about 50 million tons from Weziho, Shatüza, Mokie and other areas in Phek district of Nagaland. The exotic blocks of limestones are found in the melange zone where they are mixed with basalt which is of the pre-existing rock of ocean basin. They are the product of tectonic activity due to which they do not show any continuity.

- The subduction caused by tectonic activity dumped the limestones into the ocean where they were mixed with the basaltic material whereby causing a burnt effect to be seen in on the limestones as a result of the contact of the two. The exotic limestones are generally reported to be of Maestrichtian age.

- Geochemical data indicates that the limestones from the study area have an average CaO composition of 55.43%; and negligible content (<1-3%) of MgO and SiO_2.

- The trace elements and REE like La, Ce, Pr, Nd, Sm, Er, Gd, Tb, Dy, Ho, Yb and Lu data of the limestones values are low as compared to that of the carbonatites of igneous origin from different regions of the world and they are in agreement with those of the limestones of sedimentary origin from different regions of India.

- Further, the ratios of La/Nd, Pr/Sm. Ce/la and Ce+la/Y values from the study area coincide with the ratios of limestones of sedimentary origin from different regions of India and Russia.

- Overall study of Field relations, petrographic and geochemical indicate that the limestones of the study area are of sedimentary origin. The close association of these limestones with pelagic sediments and volcanics of the Naga Ophiolite Belt suggests their deposition in an ocean basin in a fluctuating Carbon Compensation Depth (CCD) regime.

- Geochemical data indicates that the limestones deposits are economically viable based on average composition of CaO (55.43%) and negligible content (<1-3%) of MgO and SiO_2 and estimated resources of limestones about 50 million tons from Wazeho, Shatüza, Mokie and other areas in Phek district of Nagaland which is placed above the cement grade quality as per the Indian Mineral standards.

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